A KINETIC THEORY OF SPECTRAL LINE BROADENING IN PLASMAS

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In this dissertation a formal kinetic theory is used to cast the line shape function into a form that, while similar to the "unified" theories of Smith, Cooper, and Vidal and of Voslamber, does not introduce some of the usual approximations. The resulting line shape function explicitly includes the initial correlations between the atom and perturbers, and also demonstrates the natural separation of plasma mean field and collisional effects. The classical path and no-quenching approximations are discussed and ultimately employed; however, they are not required in the formal development. The weak coupling limit is considered as a systematic approximation to the formal results. It is shown that different ways of applying this limit lead to different expressions for the memory operator, some of which correspond to existing theories. One approximation is considered which systematically incorporates the effects of electron correlations within the framework of a unified theory. In addition, a practical approximation suitable for a strongly interacting plasma is discussed.

CHAPTER I
PLASMA LINE BORADENING

I-A Introduction

For a large range of temperature and density, most of the radiation emitted by gaseous plasmas is due to atomic transitions. If individual radiators are considered to be isolated and stationary, then the width of spectral lines will only be due to natural line broadening. On the other hand if the radiators move and also interact with each other and/or the plasma, pressure and Doppler line broadening must be taken into account. In a plasma in which a significant percentage of the particles are ionized the dominant factor in pressure broadening will be Stark boradening, the understanding of which requires the study of both atomic physics and the many-body physics of plasmas.

Plasma spectroscopy has been shown to be a particularly useful diagnostic technique for laboratory and astrophysical plasmas.[1] This is due to the fact that radiation emitted by the plasma acts as a non-interfering probe, in other words, it is not necessary to disturb the radiating system in order to measure the spectrum of the emitted radiation. Impetus exists, therefore, to calculate theoretically the emitted (absorbed) line shapes. The atomic physics of light atoms is well understood, so it is the many-body theory that presents the chief obstacle. In Chapters I and II of this dissertation we discuss some of the recent approaches to this problem; in Chapters III and IV an alternative approach based on kinetic theory is proposed and developed.

I-B Causes of Line Broadening

If an excited atom or molecule were alone in a radiation field which initially contains no photons, the excited electrons could make a transition to a state of lower energy thereby emitting electromagnetic radiation with a frequency approximately equal to the energy difference between the initial and final states, in units of $\hbar$. In order to obtain a power spectrum for such a system, we consider an ensemble of excited atoms or molecules and take an ensemble average of the radiation emitted. The power spectrum thus obtained in composed of several very narrow emission lines at the characteristic natural frequencies of the atom or molecule in question. The theory describing these natural lines is discussed by Heitler[2] who points out that the widths of optical lines for atoms are on the order of 10^{-4} Angstroms.

A calculation of a line shape that includes Doppler broadening[3] requires a knowledge of the velocity distribution of the radiating atoms. This subject along with a very thorough discussion of the general line broadening problem is given by Griem.[1]

When these excited atoms or molecules are exposed to time dependent perturbations due to their interaction with other particles of the gas, degeneracies of their excited state energy levels may be removed and the half-life for a given transition may be appreciably altered.[4] This is called pressure broadening. In this case the power spectrum for the radiators in question will show a redistribution of frequencies. A typical power spectrum contains broad lines which are usually centered

near characteristic natural frequencies; hence one says that the natural lines have been broadened and perhaps slightly shifted by the perturbations.

If significant numbers of particles are ionized then the strongest of the pressure broadening mechanisms will involve the interaction of ions and electrons with the radiating particles. Since electric fields are involved this interaction is usually called Stark broadening. For atoms in many laboratory plasmas this effect is quite important, typical broadened widths being on the order of 10^3 times larger than the natural width. In fact, the broadening of spectral lines in fairly dense plasmas (e.g. 10^{16} per cm^3, 10^4 degrees K) is due almost entirely to the Stark effect which is also several orders of magnitude larger than the broadening due to neutral atom pressure broadening mechanisms.

For typical plasma conditions dealt with in this dissertation Doppler boradening[3] will only be significant near the very line center. However, this effect is easily included in the formalism developed in Chapters III and IV.

I-C Stark Broadening in Plasmas

There are two boradening agents responsible for the Stark effect in ionized gases: ions and electrons. The broadening caused by each of these is considerably different due to the difference in their velocity distributions.[4] In order to illustrate this difference, we note that the length of time which is of importance in line broadening is the half-life for the excited state of the atom. In a few half-lives we may assume that an atom, originally in an excited state,

has radiated, hence any process that takes many half-lives will be almost static from the point of view of the excited atom. It is just this fact that enables us to distinguish electrons from ions. The ions, being much heavier than the electrons, move more slowly and, for most plasma problems, the distribution of the ions does not change appreciably during a few half-lives. This is the basis for the "quasistatic" or "statistical" approximation which was developed by Holtsmark.[5,6] The method of treating the electron collisions represents an example of the opposite extreme, in which a process takes a very small fraction of a half-life and may be regarded as instantaneous. An approximation based on this limit, the impact approximation,[1,7] has been used to treat the electrons since their great speed causes most of them to pass rapidly by the atom producing collisions of very short duration compared to the excited half-life. These two limits will be discussed further in Section I-E of this dissertation.

I-D The Line Shape

The radiation spectrum of a quantum system is determined experimentally by measurement of the power radiated per unit time per unit frequency interval, averaged over the polarization and the direction of radiation.[1,4] Since this quantity has been derived many times in a variety of ways, its derivation will not be included here. The power radiated when a particle makes a spontaneous dipole transition from one quantum state to another is

$$P(\omega) = \frac{4\omega^2}{3c^3} I(\omega), \qquad \text{(I-D-1)}$$

where $I(\omega)$ is usually referred to as the line shape. It is often convenient to write $I(\omega)$ in terms of its Fourier transform $\phi(t)$,

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt e^{i\omega t}e^{-\gamma t}\Phi(t) \qquad \text{(I-D-2)}$$

$$\Phi(t)=Tr\{\vec{d}\cdot T(t)(\rho\vec{d})T^{\dagger}(t)\}. \qquad \text{(I-D-3)}$$

The damping factor, γ , which represents the effect of the natural half width of the spectral line of interest was introduced in an ad hoc manner by Smith.[4] While the effect of this term is negligible over most of the spectral line, it is a convenient quantity to introduce since it will insure the convergence of certain indeterminate integrals. $Tr\{\cdots\}$ denotes the trace operation taken over the plasma-radiator system. $\vec{d}$ is the dipole operator for the radiator and $T(t)$ is the time development operator for the system . The latter satisfies the usual equation of motion;

$$i\hbar\frac{\partial}{\partial t}T(t)=HT(t) \qquad \text{(I-D-4)}$$

and can be written formally as

$$T(t)=e^{-\frac{iHt}{\hbar}}; \qquad T(0)=1; \qquad \text{(I-D-5)}$$

where H is the Hamiltonian operator for the system, the form of which will be specified later. The density matrix for the plasma radiator system when it is in thermal equilibrium is given by

$$\rho=e^{-\beta H}/Tr\{e^{-\beta H}\}$$

$$\beta=1/K_B T \qquad \text{(I-D-6)}$$

where K_B is Boltzmann's constant and T is the temperature.

The Fourier transform of the line shape, $\Phi(t)$, can be interpreted as the autocorrelation function for the amplitude of the wave train of the radiation emitted when a radiator makes a spontaneous dipole transition.[7] An important property of $\Phi(t)$ is that

$$\Phi(-t)=[\Phi(t)]^* \tag{I-D-7}$$

which allows us to write $I(\omega)$ as a Laplace, rather than a Fourier transform,

$$I(\omega)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}e^{-\gamma t}\Phi(t). \tag{I-D-8}$$

This is an important difference since the initial value of any equation of motion may be specified more easily at $t=0$ rather than in the difficult limit $t\to-\infty$.

The Hamiltonian operator H is taken as the sum of three terms,

$$H=H_a+H_p+H_I \tag{I-D-9}$$

where H_a is the Hamiltonian for the isolated radiator, H_p is the Hamiltonian for the isolated plasma, and H_I is the Hamiltonian for the interactions between the radiator and the particles of the plasma. H_p and H_I can be further subdivided into the contributions from electrons and ions

$$H_p=H_e+H_i+H_{ie}$$

$$H_I=H_{ea}+H_{ia}\,. \tag{I-D-10}$$

It is convenient now to define the Liouville operator, L, given by[4]

$$Lf=\frac{1}{\hbar}[H,f];\quad L_af=\frac{1}{\hbar}[H_a,f];\ \text{etc.} \tag{I-D-11}$$

We can now define the Liouville time development operator,

$$e^{-iLt}f = e^{\frac{-iHt}{\hbar}} f e^{\frac{iHt}{\hbar}} = T(t) f T^{\dagger}(t) \quad . \qquad \text{(I-D-12)}$$

With this definition the autocorrelation function, given by I-D-3, becomes

$$\Phi(t) = Tr\{\vec{d} \cdot e^{-iLt} \rho \vec{d}\}. \qquad \text{(I-D-13)}$$

Equation I-D-13 is now seen to satisfy the Liouville equation, a property that will be utilized in Chapter III.

I-E Model For the Plasma

In order to evaluate equation I-D-2, additional approximations are required. There have been a number of different theoretical approaches to the problem of line broadening in plasmas, each of which has employed a different set of assumptions. In this section we will discuss a few of the approximations that are common to most of the theoretical approaches. We will further consider what restrictions these place on the model of the plasma.

No Quenching Approximation

One important approximation invoked by most theoretical calculations of a line shape is the so-called no-quenching approximation. This has been discussed in detail by many authors[1,4,7] and we will merely outline its implications here.

Any complete set of states may be used to evaluate the trace operation and the matrix elements contained in equation I-D-2. However, it is usually most convenient to use the complete set

formed by the direct product of the free radiator states denoted by $|a\rangle$ and the free plasma states denoted by $|\alpha\rangle$,

$$|a\alpha\rangle = |a\rangle|\alpha\rangle \ . \qquad \text{(I-E-1)}$$

These states satisfy the following eigenvalue equation

$$H_a|a\rangle = E_a|a\rangle$$

$$H_p|\alpha\rangle = E_\alpha|\alpha\rangle$$

$$(H_a + H_p)|a\alpha\rangle = (E_a + E_\alpha)|a\alpha\rangle \qquad \text{(I-E-2)}$$

where E_a and E_α are the energy eigenvalues for the free radiator and free plasma respectively. The initial and final states of the radiator will be denoted by $|i\rangle$ and $|f\rangle$ respectively.

The autocorrelation can be rewritten by expressing the trace as a sum over products of matrix elements,

$$\Phi(t) = \sum_{\substack{a,a',a'',a''' \\ \alpha,\alpha',\alpha'',\alpha'''}} \langle a\alpha|\vec{d}|a'\alpha'\rangle\langle a'\alpha'|T(t)|a''\alpha''\rangle\langle a''\alpha''|\rho\vec{d}|a'''\alpha'''\rangle \times \langle a'''\alpha'''|T^\dagger(t)|a\alpha\rangle . \qquad \text{(I-E-3)}$$

We shall be interested in the radiation that results when an atom spontaneously decays from some excited state of principal quantum number n to some state of lower principal quantum number n'. For low lying levels of hydrogenic atoms it is commonly assumed that radiationless transitions are improbable; hence, $T(t)$ and $T^\dagger(t)$ will be assumed to have matrix elements only between states of the same principal quantum number. This restriction, which is the no-quenching approximation, allows us to rewrite I-E-3

$$\Phi(t)=\Sigma\langle f\alpha|\vec{d}|i\alpha\rangle\langle i\alpha|T(t)|i'\alpha'\rangle\langle i'\alpha'|\rho\vec{d}|f'\alpha''\rangle\langle f'\alpha''|T^{\dagger}(t)|f\alpha\rangle \qquad (I\text{-}E\text{-}4)$$

where we have used the fact that $\vec{d}$, a pure atomic operator, will be diagonal between free plasma states.

Classical Path Approximation

For simple radiating systems for which the atomic physics is well understood the real problem that must be considered is the statistical average over perturber states. In general this is an extremely difficult problem, but one which can be simplified by employing the classical path approximation.[1,7] In this approximation the wave packets of the perturbers are assumed to be small enough so that they do not overlap either with each other or with the radiator. This allows us to view the perturbers as point particles traveling in classical trajectories and interacting with classical potentials. The effect of this approximation is to replace ρ, defined by equation I-D-6, by its classical analog and correspondingly to replace the trace over perturber states by integrals over perturber coordinates. These simplifications are probably valid for ions except at extreme densities and low temperatures, but since electrons are much lighter and their wave packets much larger they could present a problem. Several authors have shown, however, that over much of the temperature and density ranges considered by experiment the electrons will indeed behave like classical particles.[1,7]

Factoring The Initial Density Matrix

An additional approximation that is made throughout much of

the literature[1,4,7,8] is the factorization of the density matrix,

$$\rho = \rho_a \rho_i \rho_e, \qquad \text{(I-E-5)}$$

where ρ_a, ρ_i and ρ_e represent the density matrices for the radiator, the ions, and the electrons respectively. This factorization implies that the interactions among the ions, the electrons, and the radiator have been neglected. Static correlations between the ions and the electrons are not ruled out entirely, however, because they can be partially accounted for by replacing the ion-ion interactions that appear in ρ by some effective interactions which attempt to account for electron screening of the ions. On the other hand, the perturber-atom interactions are neglected in ρ; the effect of this exclusion will be discussed later. Using this factored form of the density matrix, the average over perturber coordinates in equation I-D-13,

$$\Phi(t) = \mathrm{Tr}\{\vec{d} \cdot e^{-iLt} \rho \vec{d}\}, \qquad \text{(I-E-6)}$$

can be divided into a trace over atomic coordinates and a trace over perturber coordinates

$$\Phi(t) = \mathrm{Tr}_a\{\vec{d} \cdot \mathrm{Tr}_{ie}\{e^{-iLt} \rho_i \rho_e\} \rho_a \vec{d}\}. \qquad \text{(I-E-7)}$$

Baranger[7] has shown that this approximation is equivalent to the neglect of back reaction; that is to say the trajectories of the perturbers are assumed to be unaffected by their interactions with the radiator.

Static Ion Approximation

Until recently most theories of line broadening have assumed that the ions are static: they are assumed to be so heavy that their

distribution is not appreciably altered during the radiative lifetime of the atom. This is equivalent to assuming that the ions are infinitely massive. Smith[4] has shown that this approximation implies that the kinetic energy part of the ion Hamiltonian will commute with the potential energy part. The effect of this commutation is that the free ion Hamiltonian does not appear in the Liouville time development operator in equation I-E-7. This allows us to write equation I-D-8 in the following form

$$I(\omega)=\int d\varepsilon P(\varepsilon)\tilde{J}(\omega\varepsilon) \qquad \text{(I-E-8)}$$

where

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}Tr_{ae}\{d\cdot e^{-iL(\varepsilon)t}\rho_{ae}\vec{d}\} \qquad \text{(I-E-9)}$$

and where $P(\varepsilon)$ is the static microfield distribution calculated by Hooper.[9,10] It will be noted that all of the dependence on the ion field variable is contained in the Liouville operator, $L(\varepsilon)$. The associated Hamiltonian is then given by

$$H(\varepsilon)=H_a+e\vec{\varepsilon}\cdot\vec{R}+H_e+H_{ae} \qquad \text{(I-E-10)}$$

where the ion radiator interaction is given in the dipole approximation. $\vec{R}$ is the position vector of the atomic electron and $\vec{\varepsilon}$ is the electric field strength at the radiator. For convenience in notation we will define

$$H_a(\varepsilon)=H_a+e\vec{\varepsilon}\cdot\vec{R}$$

which allows us to write

$$H(\varepsilon)=H_a(\varepsilon)+H_{ae}+H_e \qquad \text{(I-E-11)}$$

$$L(\varepsilon)=L_a(\varepsilon)+L_{ae}+L_e. \qquad \text{(I-E-12)}$$

As a result of the static ion approximation we are able to concentrate on the electron broadening of an atom placed in an external field; that is, we determine $\tilde{J}(\omega\varepsilon)$.

The effect of ion motion has been shown to be important only in the very center of a spectral line,[4] but there are, nevertheless, certain physical situations where it is observable. Several authors have discussed this problem.[11-14] It will be ignored, however, throughout the remainder of this dissertation, and the ions will henceforth be assumed to be static.

CHAPTER II
UNIFIED THEORIES

II-A Introduction

Before the late 1950's it was thought that all Stark broadening resulted from ions since the fast moving electrons were expected to have no net effect.[15] It was first shown by Kolb and Griem[16] in 1958 and by Baranger[17] that electron dynamics would be important and result in a considerable amount of broadening. Exact calculations of line profiles that include the effect of the electrons are not in general possible, hence a number of theoretical approaches have appeared, each of which uses a different set of approximations.

All line broadening theories may be divided into two broad categories, those which are fully quantum mechanical are those which make the classical path assumption for the perturbers. Several fully quantum mechanical theories have been developed; however the only successful calculations of entire line profiles have been based on theories in which the classical path approximation has been made. In the remainder of this chapter we will discuss only these theories. A fully quantum mechanical treatment, valid over the entire line shape, would be preferable, of course, but this has not yet been possible. It should be noted that the formalism developed in Chapter III of this dissertation is not limited to the classical path approximation and might be used as a starting point for an all order, fully quantum mechanical calculation.

The first line shape calculations that included electron broadening realistically were the so-called impact theories of Kolb and Griem, and of Baranger. While these approaches employ a factored density matrix and make the static ion and classical path approximations, they also make the impact approximation and the completed collision assumption. The completed collision assumption treats the electrons as moving so fast that collisions can be considered instanteous. Baranger has shown that this is equivalent to a Markov approximation that leads to a considerable simplification. Also included in the impact theory is the impact approximation. This assumes that close collisions between atom and electrons will occur one at a time and, hence, further simplifies the calculation by considering only binary electron atom collisions.

The early impact theory calculations also took the collision operator (Chapter III) to second order in the electron-atom interaction. Any theory that makes this approximation is called a second order theory. It should be pointed out that not all second order theories are impact theories: Smith and Hooper in 1967[18-20] developed a fully quantum mechanical second order theory without the completed collision or impact approximations.

It will be observed in Chapter IV that second order theories are valid only in the line center, while one-electron theories,[21] which result from expanding $\tilde{J}(\omega\varepsilon)$ in powers of the inverse frequency separation are valid only in the line wings. Recently several unified theories have been developed that are valid both in the line wings and in the line center.

II-B Unified Theory of Vidal, Cooper and Smith

The first successful unified theory calculations were carried out by Vidal, Cooper, and Smith (VCS).[22,23] Although they used the classical path and static ion approximations together with a factored density matrix they included all orders of the electron atom perturbation.

The starting point for the VCS calculation is the electron broadening line shape, given by

$$J(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}Tr_{ae}\{\vec{d}.e^{-iL(\varepsilon)t}\rho_a\rho_e\vec{d}\} \qquad \text{(II-B-1)}$$

where the approximation that $\rho_{ae}=\rho_a\rho_e$ has been utilized. The form of II-B-1 can be simplified by separating the trace over atomic coordinates from that over electron coordinates and by performing the Laplace transform:

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e Tr_a\{\vec{d}.Tr_e\{\frac{i}{\omega-L(\varepsilon)}\rho_e\}\rho_a\vec{d}\}. \qquad \text{(II-B-2)}$$

VCS then employ a projection operator technique developed by Zwanzig[24] and by Mori[25,26] to obtain the result:

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e Tr_a\{\frac{i}{\omega-L_a-\tilde{M}(\omega)}\rho_a\} \qquad \text{(II-B-3)}$$

where

$$\tilde{M}(\omega)=-i\int_0^\infty dt e^{i\Delta\omega_{op}t}\langle L_{ea}(t)G(t)L_{ea}\rangle$$

$$G(t)=T_{exp}\{-\frac{i}{h}\int_0^t dt'(1-P)L_{ea}(t')\}$$

$$\Delta\omega_{op}=\omega-L_a(\varepsilon);\quad L_{ea}(t')=e^{-i(L_a^{(\varepsilon)}+L_e)t}L_{ea}e^{i(L_a(\varepsilon)+L_e)t}. \qquad \text{(II-B-4)}$$

T is the time ordering operator and P is the projection operator defined by

$$Pf=\rho_e Tr_e\{f\}. \qquad \text{(II-B-5)}$$

In equation II-B-3 all of the complicated dependence on the N electrons has been transferred into the effective atomic operator, $M(\omega)$. This is a particularly useful functional form for the line broadening problem since $\tilde{M}(\omega)$ can be interpreted as a frequency dependent width and shift operator.[8]

Equation II-B-4 is still not a form which is amenable to calculation. One means of approximating this equation is to set the time development operator in II-B-6 equal to 1. This leads to the so-called second order theories which receive their name from the fact that $\tilde{M}(\omega)$ is second order in the electron-atom interaction. Many line broadening calculations have been made using this approximation: from the early calculations of the impact theory to a fully quantum mechanical treatment by Smith and Hooper.[18-20,] However, this approximation breaks down in the line wings. In other words when L_{ea} and therefore, $\tilde{M}(\omega)$, is large, it is incorrect to stop at finite order in an electron-atom perturbation expansion.

Since the unified theory is supposed to be valid in the line wings as well as in the line center, setting the time development operator equal to 1 is not allowable. VCS showed that to lowest order in the density the time development operator could be approximated in the following way;

$$G(t)=T\exp\{-\frac{i}{\hbar}\int_0^t dt' e^{-iL_e t}(1-P)\sum_j L_{ea}(j)e^{iL_e t}\}$$
$$\approx \prod_j T\exp\{-\frac{i}{\hbar}\int_0^t dt' L_{ea}(j,t')\} \qquad \text{(II-B-6)}$$

with $\tilde{M}(\omega)$ given by

$$\tilde{M}(\omega)=-iN\int dt e^{i\Delta\omega_{op}t}\langle L_{ea}(1,t)T_{exp}\{-\frac{i}{\hbar}\int_0^t dt' L_{ea}(1,t')\}L_{ea}(1). \quad \text{(II-B-7)}$$

The average is performed over the coordinates of particle 1 only. It should be noted that II-B-7 is all orders in the electron-atom interaction. It was shown that in this approximation

$$(1-P)L_{ea}(1)\rightarrow L_{ea}(1). \quad \text{(II-B-8)}$$

One important limitation imposed by taking only the lowest order term in the density expansion is that electron-electron interactions are omitted both from ρ and $L_{ea}(j,t)$. VCS partially correct for this by assuming that the electrons can be replaced by shielded quasi-particles, in other words they assume that the electric field in $\varepsilon \cdot \vec{R}$ is shielded. We will see in the next section how Capes and Voslamber included electron-electron correlations in their theory.

Another VCS approximation, the neglect of time ordering from equation II-B-7, has been discussed in detail by Smith, Cooper, and Roszman,[28] and it will not be further considered here. Integrating by parts, equation II-B-7 becomes

$$\tilde{M}(\omega)=-i\hbar\Delta\omega_{op}\int dt e^{i\Delta\omega_{op}t}\langle \exp\{-\frac{i}{\hbar}\int_0^t dt' L_{ea}(1,t')\}-1\rangle_{\Delta\omega_{op}}. \quad \text{(II-B-9)}$$

Finally VCS assume that the time dependence of R can be neglected in the expression for $L_{ea}(1,t)$; hence

$$L_{ea}(1,t)=e\vec{R}\cdot e^{-iL_e(1)t}\vec{\varepsilon}(1)e^{iL_e(1)t}. \quad \text{(II-B-10)}$$

Instead of actually performing a spatial integration over the time dependent shielded electric field, $e^{-iL_e(1)t}\vec{\varepsilon}(1)e^{iL_e(1)t}$, VCS replace it by an unshielded one and cut off the resulting integral over the free particle trajectories at the Debye sphere. It is interesting to note that if the upper limit of the integral in the exponential of II-B-9 is extended to infinity, the time development operator in the interaction representation goes over to the S-matrix and we regain an all order impact theory. This is entirely equivalent to the completed collision assumption. Thus the expression for $\tilde{M}(\omega)$ finally evaluated by VCS was

$$\tilde{M}(\omega)=-in\Delta\omega_{op}\int dt e^{i\Delta\omega_{op}t}\langle\exp\{-\frac{i}{\hbar}\int_0^t dt' L_{ea}(\vec{r}+\vec{v}\,t')\}-1\rangle_{\Delta\omega_{op}}. \quad \text{(II-B-11)}$$

The resulting matrix was inverted to yield an expression for the line shape.

The numerical results obtained by this formulation of the line broadening problem has been shown to agree well with most currently available experimental results. Nevertheless, the approximations that have gone into this development are not entirely transparent. The density expansion was truncated in a way that precludes the possibility of going to higher order. In addition, there is no way of examining the validity of the way in which electron correlations were included.

It is also possible to formulate a systematic kinetic theory approach to line broadening. This method, as developed by Capes and Voslamber,[27,29] will be discussed in the next section.

II-C Theory of Capes and Voslamber

A systematic treatment of the line broadening problem may be effected by viewing the radiating atom and the N electrons as an N+1 particle system obeying a Liouville equation. Capes and Voslamber[27,29] have developed such a theory that included electron correlations in a more systematic fashion. This section will outline their approach, indicating its advantages and where it differs from the VCS theory.

Capes and Voslamber make several of the usual approximations including the classical path approximation, the neglect of perturber-atom interactions from the density matrix, and the static ion approximation. They do not, however, neglect electron correlations, and their theory offers an understanding of what effect these correlations will have on the line shape.

As in the VCS theory, Capes and Voslamber start with the equation

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^t dt e^{i\omega t}Tr_a\{\vec{d}\cdot Tr_e\{e^{-iL(\varepsilon)t}\rho_e\}\rho_a\vec{d}\} \qquad \text{(II-C-1)}$$

which they reduce to a simpler form by utilizing the fact that the integrand obeys a Liouville equation:

$$\left(\frac{\partial}{\partial t}+iL_a+i\Sigma_j L_{ea}(j)\right)\vec{D}(a,1\cdots N;t)+\left(\Sigma_j \vec{v}_j\cdot\vec{\nabla}_j-\frac{1}{m}\frac{\partial\omega}{\partial\vec{x}_j}\cdot\frac{\partial}{\partial\vec{v}_j}\right)\vec{D}(a,1\cdots N;t)=0$$

$$\omega_j=\Sigma_j\phi_{jk};\quad \phi_{jk}=-\frac{e^2}{|\vec{r}_j-\vec{r}_k|} \qquad \text{(II-C-2)}$$

where we have defined

$$\vec{D}(a,1\cdots N;t)=V^N e^{-iL(\varepsilon)t}\rho_e\rho_a\vec{d}, \qquad \text{(II-C-3)}$$

and where we have explictly made the classical path approximation. Taking partial traces of II-C-2, a BBGKY hierarchy of kinetic equations results

$$\left(\frac{\partial}{\partial t}+iL_a+i\sum_{j=1}^{s}L_{ea}(j)\right)\vec{D}(a,1\cdots s;t)+\sum_{j=1}^{s}\left(\vec{v}_j\cdot\vec{\nabla}_j-\frac{1}{m}\sum_{i=s+1}^{N}\frac{\partial\phi_{ij}}{\partial\vec{x}_j}\cdot\frac{\partial}{\partial\vec{v}_j}\right)\vec{D}(a,1\cdots s;t)$$

$$=-in\int d(s+1)L_{ea}(s+1)\vec{D}(a,1\cdots s;s+1;t)-\frac{n}{m}\int d(s+1)\sum_{i=1}^{s}\frac{\partial\phi_{s+1,i}}{\partial\vec{x}_i}\cdot\frac{\partial}{\partial\vec{v}_i}\vec{D}(a,1\cdots s;t) \quad \text{(II-C-4)}$$

where

$$\vec{D}(a,1\cdots s;t)\equiv Tr_{s+1\cdots N}\{\vec{D}(a,1\cdots N;t)\}. \quad \text{(II-C-5)}$$

The first two equations of this hierarchy are

$$\left(\frac{\partial}{\partial t}+iL_a\right)\vec{D}(a;t)=-in\int d(2)\vec{D}(a,1;t), \quad \text{(II-C-6)}$$

$$\left(\frac{\partial}{\partial t}+iL_a+iL_{ea}(1)\right)+\vec{v}_1\cdot\vec{\nabla}_1)\vec{D}(a,1;t)=-in\int d(2)L_{ea}(2)\vec{D}(a,1,2;t)$$

$$-i\frac{n}{m}\int d(2)\frac{\partial\phi_{21}}{\partial\vec{x}_1}\cdot\frac{\partial}{\partial\vec{v}_1}\vec{D}(a,1,2;t). \quad \text{(II-C-7)}$$

Since $\tilde{J}(\omega\varepsilon)$ could be written as

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int dt e^{i\omega t}Tr_a\{\vec{d}\cdot\vec{D}(a;t)\}, \quad \text{(II-C-8)}$$

Capes and Voslamber then solved for $\vec{D}(a;t)$. To do so they assumed that $\vec{D}(a,1,2;t)$ could be expressed as an approximate functional of $\vec{D}(a;t)$ and $\vec{D}(a,1;t)$. This resulted in a pair of coupled differential equations which were solved simultaneously. Their closure relationship based on the weak coupling approximation was

$$\vec{D}(a,1,2;t)=\vec{D}(a,1;t)V_\rho(2)+\vec{D}(a,1;t)V_\rho(1)+\vec{D}(a;t)V^2(\rho(12)-\rho(1)\rho(2)) \quad \text{(II-C-9)}$$

where the reduced density matrix is given by[30]

$$\rho(1\cdots s)=\int\cdots\int d(s+1)\cdots d(N)\rho_e .$$

If the closure relationship, II-C-9, is substituted into the second equation of the hierarchy, II-C-7, and if only those terms which are lowest order in an expansion in the electron-electron coupling strength are kept, then II-C-7 becomes

$$\left(\frac{\partial}{\partial t}+iL_a+iL_{ea}(1)+\vec{v}_1\cdot\vec{\nabla}_1\right)\vec{D}(a,1;t)=-\frac{n}{m}\frac{\partial f_0(v_1)}{\partial \vec{v}_1}\int d(2)\,\frac{\partial \phi_{21}}{\partial \vec{x}_1}\vec{D}(a,1;t)$$

$$-inf_0(v_1)\int d(2)L_{ea}(2)\vec{D}(a,2;t)-nf_0(v_1)\int d(2)L_{ea}(2)g(12)\rho(2)\vec{D}(a;t);$$

$$\rho(12)=\rho(1)\rho(2)g(12);\quad f_0(v_1)=V\rho(1), \tag{II-C-10}$$

where the symmetry properties of the interactions have been used to eliminate some of the resulting integrals. The first term on the right hand side of equation II-C-10 is recognized as the Vlasov operator, V(1).[27] If the Laplace transforms of II-C-6 and II-C-10 are solved simultaneously, we find that

$$\tilde{\vec{D}}(a,1;\omega)=\frac{i}{\omega-L_a-L_{ea}(1)+i\vec{v}_1\cdot\vec{\nabla}_1-V(1)}L^s_{ea}(1)\vec{D}(a;\omega); \tag{II-C-11}$$

V(1) is again the Vlasov operator, and L^s_{ea} is the electron-atom interaction, statically shielded by the electron-electron pair correlation function. If equation II-C-11 is substituted into the right hand side of the Laplace transform of II-C-5 then we get

$$\tilde{\vec{D}}(a,1;\omega)=\frac{i}{\omega-L_a-M(\omega)}\rho_a\vec{d} \tag{II-C-12}$$

where the memory operator, $\tilde{M}(\omega)$, is given by

$$\tilde{M}(\omega)=-in\int d(1)L_{ea}(1)\frac{i}{\omega-L_a-L_{ea}(1)+i\vec{v}_1\cdot\vec{\nabla}_1-V(1)}L^s_{ea}(1). \qquad \text{(II-C-13)}$$

Using a technique similar to the one presented in Appendix F Capes and Voslamber showed that this equation reduces to

$$\tilde{M}(\omega)=-iN\int d(1)\frac{1}{2\pi}\int dt e^{i\Delta\omega_{op}t}L^D_{ea}(1,t)U(t)L^s_{ea}(1)$$

$$U(t)=T_{exp}\{-\frac{i}{\hbar}\int_0^t dt' L_{ea}(1,t')\} \qquad \text{(II-C-14)}$$

where $L^D_{ea}(1,t)$ is a dynamically shielded interaction and $U(t)$ is the interaction representation time development operator. This result is identical to that of VCS except for the shielding which appears in the electron-atom interactions. Note, however, that the electron-electron interaction appearing in $U(t)$ is not shielded while the two interactions appearing around it are. Thus it is not possible to further simplify II-C-14 by performing an integration by parts as was done in equation II-B-10.

The main strength of the approach of Capes and Voslamber is the fact that their theory includes the effect of electron correlations in a way which is preferable to the ad hoc cut-off procedure employed by VCS. Its main weakness, however, is the closure hypothesis, equation II-C-7. Capes and Voslamber show that this is closely related to the impact approximation (binary collision approximation for electron-atom interactions, and like the impact approximation, there is no clear cut way of improving upon it. In the next chapters we will close the hierarchy in a

way in which approximations may be more systematically made, and we will suggest an approximation procedure which leads to a more inclusive result than found in equation II-C-14.

CHAPTER III
FORMAL KINETIC THEORY APPLIED TO LINE BROADENING

III-A The Hierarchy

In this section we will develop a kinetic theory of line broadening in plasmas similar to that derived by Voslamber.[27,29] The formalism will be developed for an atom, perturbed by an external field, and immersed in a one component plasma; therefore the static ion approximation is implicit. However, two other frequently employed approximations will be avoided: the classical path approximation and the neglect of electron-atom interactions in the initial density matrix.

From equation I-E-9 the line shape function for electron broadening is given by

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}Tr_{ae}\{\vec{d}\cdot e^{-iL(\varepsilon)t}\rho_{aN}\vec{d}\}$$

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_eTr_{ae}\{\vec{d}\cdot\frac{i}{\omega-L(\varepsilon)}\rho_{aN}\vec{d}\}\ . \qquad \text{(III-A-1)}$$

This can be written in the alternative form:

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}Tr_{ae}\{\vec{d}\cdot\frac{1}{V^N}\vec{D}(a,1\cdots N;t)\}$$

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_eTr_{ae}\{\vec{d}\cdot\frac{1}{V^N}\tilde{\vec{D}}(a,1\cdots N;\omega)\} \qquad \text{(III-A-2)}$$

where we have defined the operator $\vec{D}(a,1\cdots N;t)$ and its Laplace transform, $\tilde{\vec{D}}(a,1\cdots N;\omega)$, as in equation II-C-3;

$$\vec{D}(a,1\cdots N;t)=V^N e^{-iL(\varepsilon)t}\rho_{aN}\vec{d}$$

$$\tilde{\vec{D}}(a,1\cdots N;\omega)=V^N \frac{i}{\omega-L(\varepsilon)}\rho_{aN}\vec{d} \qquad \text{(III-A-3)}$$

where V is the system volume and ρ_{aN} is given by

$$\rho_{aN}=e^{-\beta H(\varepsilon)}/Tr\{e^{-\beta H(\varepsilon)}\},$$

$$H(\varepsilon)=H_a(\varepsilon)+\sum_j H_e(j)+\sum_{i<j} H_{ee}^{ij}+\sum_j H_{ea}(j).$$

In the above equation $H_e(j)$ represents the kinetic energy of particle j, H_{ee}^{ij} represents the interaction between particles i and j, and $H_{ea}(j)$ represents the interaction of the atom with electron j. The Liouville operator corresponding to $H(\varepsilon)$ is given by

$$L=L_a+\sum_j L_e(j)+\sum_{i<j} L_{ee}^{ij}+\sum_j L_{ea}(j) \qquad \text{(III-A-4)}$$

where here and henceforth the functional dependence of L and L_a on the ion microfield, ε, will be suppressed. We also define the reduced functions,

$$\vec{D}(a,1\cdots s;t)=V^s Tr_{s+1\cdots N}\{e^{-iLt}\rho_a\vec{d}\},$$

$$\tilde{\vec{D}}(a,1\cdots s;\ )=V^s Tr_{s+1\cdots N}\{\frac{i}{\omega-L}\rho_a\vec{d}\},$$

$$\rho(a,1\cdots s)=Tr_{s+1}\{\rho_{aN}\}. \qquad \text{(III-A-5)}$$

Hence the expression for $\tilde{J}(\omega\varepsilon)$ can be written as

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e\int_0^\infty dt e^{i\omega t}Tr_a\{\vec{d}\cdot\vec{D}(a;t)\},$$

$$\tilde{J}(\omega\varepsilon)=\frac{1}{\pi}R_e Tr_a\{\vec{d}\cdot\tilde{\vec{D}}(a;\omega)\}, \qquad \text{(III-A-6)}$$

and thus the problem is to determine $\vec{D}(a;t)$ or $\tilde{\vec{D}}(a;\omega)$.

We start by noting that the operator $\vec{D}(a,1\cdots N;t)$ obeys the Liouville equation,[31]

$$\left(\frac{\partial}{\partial t}+iL\right)\vec{D}(a,1\cdots N;t)=0, \tag{III-A-7}$$

from which we can now generate a hierarchy of kinetic equations by taking partial traces;

$$\left(\frac{\partial}{\partial t}+iL^{(s)}\right)\vec{D}(a,1\cdots s;t)=-in\sum_{i=1}^{s}Tr_{s+1\cdots N}\{(L_{ea}(s+1)+L_{ee}^{i,s+1})\vec{D}(a,1\cdots s+1;t)\} \tag{III-A-8}$$

$$L^{s}=L_{a}+\sum_{j=1}^{s}L_{e}(j)+\sum_{j=1}^{s}L_{ea}(j)+\sum_{i<j\leq s}L_{ee}^{ij} \tag{III-A-9}$$

where the thermodynamic limit has been assumed. The first three equations of this hierarchy are given explicitly:

$$\left(\frac{\partial}{\partial t}+iL_{a}\right)\vec{D}(a;t)=-inTr_{1}\{L_{ea}(1)\vec{D}(a,1;t)\},$$

$$\left(\frac{\partial}{\partial t}+iL^{(1)}\right)\vec{D}(a,1;t)=-inTr_{2}\{(L_{ee}(2)+L_{ee}^{21})\vec{D}(a,1,2;t)\},$$

$$\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\vec{D}(a,1,2;t)=-inTr_{3}\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\vec{D}(a,1,2,3;t)\}. \tag{III-A-10}$$

The approach followed by Capes and Voslamber to solve for $\vec{D}(a;t)$ was to use a closure relationship, expressing $\vec{D}(a,1,2;t)$ as an approximate functional of $\vec{D}(a;t)$ and $\vec{D}(a,1;t)$. While this procedure led to a closed set of coupled differential equations that could be readily solved, its weakness lay in the nature of the closure relationship. They justify their method of closure by relating it to an expansion in the coupling parameters; but the limitations of

their technique are not clear and a method of improving upon their results is not obvious.

The procedure followed by Vidal, Cooper, and Smith[22,23] was not as inclusive as the one used by Capes and Voslamber, but it does have one important advantage: the expansion in the density, used in order to get an expression for the memory operator, is well understood and can be related to a diagrammatic expansion of the self-energy operator.

In this dissertation we combine the advantages of the hierarchy approach of Capes and Voslamber with those of the weak coupling limit. In the remainder of this chapter we will develop a formally exact method to close the hierarchy.[32,33] In Chapter IV we will apply the weak coupling limit to the formally exact expression for $\vec{D}(a;t)$. It will be seen in Chapter IV that, depending on how the weak coupling limit is applied, we can reproduce several of the existing theories of electron broadening as approximations to the exact theory. Furthermore, we then generate our own approximation procedure which enables us to develop a more systematic theory.

III-B Formal Closure

First Equation of the Hierarchy

Rather than immediately employ an approximate closure relationship, we will proceed formally to obtain an exact relationship by observing that $\vec{D}(a,1,\cdots s;t)$ represents a linear map of an atomic function onto a space containing functions of electron coordinates as well as atomic coordinates;

$$\vec{D}(a,1\cdots s;t)=U(a,1\cdots s;t)\rho(a)\vec{d},$$

$$\tilde{\vec{D}}(a,1\cdots s;\omega)=U(a,1\cdots s;\omega)\rho(a)\vec{d}, \qquad \text{(III-B-1)}$$

$$U(a,1\cdots s;t)=Tr_{s+1\cdots N}\{V^N e^{-iLt}\rho_{aN}\}\rho^{-1}(a),$$

$$\tilde{U}(a,1\cdots s;\omega)=Tr_{s+1\cdots N}\{V^N \frac{i}{\omega-L}\rho_{aN}\}\rho^{-1}(a). \qquad \text{(III-B-2)}$$

For the specific case where the trace is taken over all N electrons we get

$$\vec{D}(a;t)=U(a;t)\rho(a)\vec{d},$$

$$\tilde{\vec{D}}(a;\omega)=\tilde{U}(a;\omega)\rho(a)\vec{d}, \qquad \text{(III-B-3)}$$

$$U(a;t)=Tr_{1\cdots N}\{V^N e^{-iLt}\rho_{aN}\}\rho^{-1}(a),$$

$$\tilde{U}(a;\omega)=Tr_{1\cdots N}\{V^N \frac{i}{\omega-L}\rho_{aN}\}\rho^{-1}(a). \qquad \text{(III-B-4)}$$

The first step in effecting our closure will be to eliminate $\rho(a)\vec{d}$ in III-B-1 in favor of $\vec{D}(a;t)$ in equation III-B-3. Hence, assuming that an inverse exists for $U(a;t)$ and $\tilde{U}(a;\omega)$, the functionals which result are

$$\vec{D}(a,1\cdots s;t|\vec{D}(a;t))=U(a,1\cdots s;t)U^{-1}(a;t)\vec{D}(a;t), \qquad \text{(III-B-5)}$$

or the Laplace transformed version,

$$\tilde{\vec{D}}(a,1\cdots s;\omega|\tilde{\vec{D}}(a;\omega))=\tilde{U}(a,1\cdots s;\omega)U^{-1}(a;\omega)\tilde{\vec{D}}(a;\omega). \qquad \text{(III-B-6)}$$

$U(a,1\cdots s;t)$ and $\tilde{U}(a,1\cdots s;\omega)\tilde{U}^{-1}(a;\omega)$ will in general be extremely complicated operators. Equation III-B-5 gives us a formal method

of closing the hierarchy of equations at any level (any value of s).

The first equation of the hierarchy, III-A-10, may therefore be written

$$(\frac{\partial}{\partial t}+iL_a)\vec{D}(a;t)=-inTr_1\{L_{ea}(1)U(a,1;t)U^{-1}(a;t)\}\vec{D}(a;t). \qquad \text{(III-B-7)}$$

This can be cast in a different form,[34]

$$(\frac{\partial}{\partial t}+iL_a)\vec{D}(a;t)=-i\int_0^t dt'\chi(t'-t)\vec{D}(a;t) \qquad \text{(III-B-8)}$$

by introducing a collision operator, $\chi(t'-t)$, which is non-local in time. This is a particularly easy form to Laplace transform. Inspection of equation III-B-5 shows that as $t\to 0$, $\vec{D}(a,1\cdots s;t)$ approaches a time independent functional of $\vec{D}(a;t)$

$$\lim_{t\to 0}\vec{D}(a,1\cdots s;t|\vec{D}(a;t)=\vec{D}(a,1\cdots s;t=0|\vec{D}(a;t))$$

$$=U(a,1\cdots s;t=0)U^{-1}(a;t=0)\vec{D}(a;t). \qquad \text{(III-B-9)}$$

This shows that $\chi(t'-t)$ has a singular contribution at $t'=t$. Extracting this part explicitly from $\chi(t'-t)$ yields

$$(\frac{\partial}{\partial t}+iL_a)\vec{D}(a;t)=-iB\vec{D}(a;t)-i\int_0^t dt'M(t'-t)\vec{D}(a;t') \qquad \text{(III-B-10)}$$

where B is time independent. The operator $M(t'-t)$ is now non-singular and the integral in which it appears vanishes as $t\to 0$. If equation III-B-10 is Laplace transformed we find that

$$(\omega-L_a)\tilde{\vec{D}}(a;\omega)=i\vec{D}(a;t=0)+\tilde{M}(\omega)\tilde{\vec{D}}(a;\omega)+B\tilde{\vec{D}}(a;\omega)$$

$$\tilde{\vec{D}}(a;\omega)=\frac{i}{\omega-L_a-B-M(\omega)}\rho_a\vec{d}. \qquad \text{(III-B-11)}$$

This result displays the same functional form obtained by VCS where $\tilde{M}(\omega)$ together with B plays the role of the VCS memory operator. It can be shown that B vanishes when electron-atom interactions are neglected from the density matrix. Consistent with the separation of the singular part of the collision operator, $\chi(t'-t)$, from the non-singular part, we write $\vec{D}(a,1\cdots s;t|\vec{D}(a;t))$ as the sum of its short time limit, equation III-B-9, and a time dependent remainder which vanishes at t=0:

$$\vec{D}(a,1\cdots s;t|\vec{D}(a;t))=U(a,1\cdots s;t=0)U^{-1}(a;t=0)\vec{D}(a;t)+\vec{P}(a,1\cdots s;t) \quad \text{(III-B-12)}$$

where

$$\vec{P}(a,1\cdots s;t=0)=0 . \quad \text{(III-B-13)}$$

It can be seen that $\vec{P}(a,1;t)$ is related to the non-singular part of the collision operator, $\chi(t'-t)$. Equation III-B-9, which is sometimes called the short time limit, is discussed in Section C of this chapter.

We now make a few observations about $\vec{D}(a,1\cdots s;t=0|\vec{D}(a;t))$ and $\vec{P}(a,1\cdots s;t)$, given by equations III-B-9 and III-B-12. From the definition of $U(a,1\cdots s;t)$ given by III-B-2 we have

$$U(a,1\cdots s;t=0)=\rho(a,1\cdots s)\rho^{-1}(a);\ U(a,t=0)=1$$

$$U(a,1\cdots s;t=0)U^{-1}(a,t=0)=\rho(a,1\cdots s)\rho^{-1}(a) . \quad \text{(III-B-14)}$$

Substituting III-B-14 into III-B-12 and taking the Laplace transform gives

$$\tilde{\vec{D}}(a,1\cdots s;\omega|\tilde{\vec{D}}(a;\omega)=\rho(a,1\cdots s)\rho^{-1}(a)\tilde{\vec{D}}(a;\omega)+\tilde{\vec{P}}(a,1\cdots s;\omega). \quad \text{(III-B-15)}$$

The closure relationship, equation III-B-6 in conjunction with equation III-B-15 enables us to write:

$$\tilde{\vec{P}}(a,1\cdots s;\omega)=\tilde{K}(a,1\cdots s;\omega)\tilde{\vec{D}}(a;\omega) \qquad \text{(III-B-16)}$$

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{U}(a,1\cdots s;\omega)\tilde{U}^{-1}(a;\omega)-\rho(a,1\cdots s)\rho^{-1}(a). \qquad \text{(III-B-17)}$$

The functional form of the operators, B and $\tilde{M}(\omega)$, can now be exhibited explicitly. Considering the Laplace transform of the first equation of the hierarchy, equation III-A-10,

$$(\omega-L_a)\tilde{\vec{D}}(a;\omega)-nTr_1\{L_{ea}(1)\tilde{\vec{D}}(a,1;\omega)\}=i\rho(a)\vec{d}$$

and by using equations III-B-15 and III-B-16 we arrive at

$$(\omega-L_a)\tilde{\vec{D}}(a;\omega)-nTr_1\{L_{ea}(1)\rho(a,1)\rho^{-1}(a)\}\tilde{\vec{D}}(a;\omega)$$

$$-nTr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\}\tilde{\vec{D}}(a;\omega)=i\rho(a)\vec{d}\,. \qquad \text{(III-B-18)}$$

This can be compared to equation III-B-11 to get

$$\tilde{\vec{D}}(a;\omega)=\frac{i}{\omega-L_a-B-\tilde{M}(\omega)}\rho(a)\vec{d}$$

$$B=nTr_1\{L_{ea}(1)\rho(a,1)\rho^{-1}(a)\}$$

$$\tilde{M}(\omega)=nTr_1\{L_{ea}(1)\tilde{\vec{D}}(a,1;\omega)\}\,. \qquad \text{(III-B-19)}$$

The operator, B, as it is defined in equation III-B-19, is a simple function of well defined operators and can be calculated. The operator $\tilde{M}(\omega)$, on the other hand, contains the formal operator, $\tilde{K}(a,1;\omega)$, which is obtained from the next equation of the hierarchy.

Second Equation of the Hierarchy

The approach used to cast the first equation of the hierarchy in the form of a linear kinetic equation is well known. However, it has been shown that if we close the second equation of the hierarchy in the same manner as the first, a useful result, which may be easily and systematically approximated, is obtained.[32,33] The approximation technique used will be discussed in detail in Chapter IV.

From equation III-A-10 we have the second equation of the hierarchy,

$$(\frac{\partial}{\partial t}+iL^{(1)})\vec{D}(a,1;t)=-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{D}(a,1,2;t)\}.$$

In order to put this into a form where $\tilde{K}(a,1;\omega)$ appears explicitly, we first use equation III-B-15:

$$\vec{D}(a,1;t)=\rho(a,1)\rho^{-1}(a)\vec{D}(a;t)+\vec{P}(a,1;t)$$

$$\vec{D}(a,1,2;t)=\rho(a,1,2)\rho^{-1}(a)\vec{D}(a;t)+\vec{P}(a,1,2;t). \qquad \text{(III-B-20)}$$

If these relations are substituted into equation III-B-20 the resulting expression is

$$(\frac{\partial}{\partial t}+iL^{(1)})\rho(a,1)\rho^{-1}(a)\vec{D}(a;t)+(\frac{\partial}{\partial t}+iL^{(1)})\vec{P}(a,1;t)$$
$$=-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\rho(a,1,2)\rho^{-1}(a)\}\vec{D}(a;t)$$
$$-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{P}(a,1,2;t)\}. \qquad \text{(III-B-21)}$$

This equation is developed further in Appendix A where the properties of the equilibrium hierarchy for an N+1 particle system

are used.[30] The resulting kinetic equation is

$$\left(\frac{\partial}{\partial t}+iL^{(1)}\right)\vec{P}(a,1;t)=-iGL_{ea}(1)\rho^{-1}(a)\vec{D}(a;t)+i\rho(a,1)\times$$

$$\times\rho^{-1}(a)nTr_1\{L_{ea}(1)\vec{P}(a,1;t)\}-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{P}(a,1,2;t)\} \quad \text{(III-B-22)}$$

where the operator $GL_{ea}(1)$ is given by

$$GL_{ea}(1)\rho^{-1}(a)\vec{D}(a;t)=[\rho(a,1)-n\rho(a,1)\rho^{-1}(a)nTr_2\{\rho(a,2)P_{21}\}$$

$$+nTr_2\{\rho(a,1,2)P_{21}\}]L_{ea}(1)\rho^{-1}(a)\vec{D}(a;t) \quad \text{(III-B-23)}$$

and where P_{ij} is the permutation operator, defined in Appendix A.

Taking the transform of equation III-B-22 we have

$$(\omega-L^{(1)})\tilde{\vec{P}}(a,1;\omega)+\rho(a,1)\rho^{-1}(a)nTr_1\{L_{ea}(1)\tilde{\vec{P}}(a,1;\omega)\}$$

$$-nTr_2\{(L_{ea}(2)+L_{ee}^{21})\tilde{\vec{P}}(a,1,2;\omega)\}=GL_{ea}(1)\tilde{\vec{D}}(a;\omega) \quad \text{(III-B-24)}$$

where we have used equation III-B-13. If we use the definition that $\tilde{\vec{P}}(a,1\cdots s;\omega)=\tilde{K}(a,1\cdots s;\omega)\tilde{\vec{D}}(a;\omega)$ then equation III-B-24 becomes

$$(\omega-L^{(1)})\tilde{\vec{K}}(a,1;\omega)+\rho(a,1)\rho^{-1}(a)nTr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\}$$

$$-nTr_2\{(L_{ea}(2)+L_{ee}^{21})\tilde{\vec{K}}(a,1,2;\omega)=GL_{ea}(1). \quad \text{(III-B-25)}$$

Thus we have a kinetic equation for $\tilde{K}(a,1;\omega)$ in terms of $\tilde{K}(a,1,2;\omega)$ and a source term, $GL_{ea}(1)$. We now make the formal definition

$$\tilde{V}(a,1;\omega)\hat{\tilde{K}}(a,1;\omega)=nTr_2\{(L_{ea}(2)+L_{ee}^{21})\hat{\tilde{K}}(a,1,2;\omega)\}$$

$$-\rho(a,1)\rho^{-1}(a)nTr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\} \quad \text{(III-B-26)}$$

which is discussed in Appendix B. With the use of equation III-B-26

we solve equation III-B-25 formally to get a convenient form for $\tilde{K}(a,1;\omega)$

$$\tilde{K}(a,1;\omega)=\frac{1}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}GL_{ea}(1)\ . \qquad \text{(III-B-27)}$$

The memory operator then becomes

$$\tilde{M}(\omega)=-inTr_1\{L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}\tilde{GL}_{ea}(1)\}. \qquad \text{(III-B-28)}$$

It is now possible to analyze $\tilde{V}(a,1;\omega)$ in exactly the same manner that we analyzed the collision operator, $\chi(t'-t)$, that is, we separate $\tilde{V}(a,1;\omega)$ into frequency dependent and frequency independent parts:

$$\tilde{V}(a,1;\omega)=\tilde{V}(a,1;\omega=\infty)+\tilde{V}_c(a,1;\omega)\ . \qquad \text{(III-B-29)}$$

The infinite frequency term, $V(a,1;\omega=\infty)$, is analyzed in Appendix B with the result that

$$\tilde{V}(a,1;\omega=\infty)\tilde{K}(a,1;\omega)=nTr_2\{(L_{ea}(2)+L_{ee}^{21})\times$$

$$\times\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\}\tilde{K}(a,1;\omega)-\rho(a,1)\rho^{-1}(a)Tr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\}$$

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)L_{ea}(1). \qquad \text{(III-B-30)}$$

The collisional part of III-B-29 can best by analyzed by continuing to the next equation of the hierarchy.

Third Equation of the Hierarchy

We already have expressions for $\tilde{M}(\omega)$ and $\tilde{J}(\omega\varepsilon)$ in terms of $V(a,1;\omega=\infty)$ which are formally more inclusive than any previously derived. In order to fully understand what part of $\tilde{V}(a,1;\omega)$ is included in its short time limit, $V(a,1;\omega=\infty)$, we must understand what is excluded from it; that is, we must look at $\tilde{V}_c(a,1;\omega)$. To do this we will require the third equation of the hierarchy,

$$(\frac{\partial}{\partial t}+iL^{(2)})\vec{D}(a,1,2;t)-inTr_3\{(L_{ea}(3)+L^{32}_{ee}+L^{31}_{ee})\vec{D}(a,1,2,3;t)\}. \quad \text{(III-A-10)}$$

From Appendix B, equations B-9 and B-10, we know that:

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)L_{ea}(1)\rho^{\,1}(a)$$

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)\tilde{\mathcal{K}}^{\,1}(a,1;\omega)\tilde{K}(a,1;\omega). \quad \text{(III-B-31)}$$

Then in equation B-11 we defined the operator $\tilde{V}(a,1;\omega)$:

$$\tilde{V}(a,1;\omega)\tilde{K}(a,1;\omega)=nTr_2\{(L_{ea}(2)+L^{21}_{ee})\tilde{\mathcal{K}}(a,1,2;\omega)\tilde{\mathcal{K}}(a,1;\omega)\}\tilde{K}(a,1;\omega)$$

$$-\rho(a,1)\rho^{\,1}(a)NTr_2\{L_{ea}(2)P_{21}\}\tilde{K}(a,1;\omega). \quad \text{(III-B-11)}$$

We now want to divide $\tilde{V}(a,1;\omega)$ into frequency dependent and independent parts, in a manner suggestive of the separation of the collision operator in equation III-B-11. In order to do this we consider the inverse transform of $\tilde{K}(a,1\cdots s;\omega)$ and write it as a functional of the inverse transform of $\tilde{K}(a,1;\omega)$,

$$K(a,1\cdots s;t)=K(a,1\cdots s;t|K(a,1;t)). \quad \text{(III-B-32)}$$

Following a procedure analogous to that used to derive equation III-B-12 we now separate this last expression into a short time functional and a time dependent remainder term:

$$K(a,1\cdots s;t|K(a,1;t))=K(a,1\cdots s;t=0|K(a,1;t))+X(a,1\cdots s;t). \qquad \text{(III-B-33)}$$

The Laplace transform of equation III-B-33 yields

$$\tilde{K}(a,1\cdots s;\omega|\tilde{K}(a,1;\omega))=K(a,1\cdots s;t=0|\tilde{K}(a,1;\omega))+\tilde{X}(a,1\cdots s;\omega). \qquad \text{(III-B-34)}$$

Hence, comparing this result with equation B-13, we observe that the infinite frequency limit is related to the short time limit:

$$\tilde{K}(a,1\cdots s;\omega|\tilde{K}(a,1;\omega))=\mathcal{K}(a,1\cdots s;\omega=\infty)\,\mathcal{K}^{-1}(a,1;\omega=\infty)\tilde{K}(a,1;\omega)$$
$$+\tilde{X}(a,1\cdots s;\omega) \qquad \text{(III-B-35)}$$

$$\tilde{X}(a,1\cdots s;\omega)=\tilde{\chi}(a,1\cdots s;\omega)\tilde{K}(a,1;\omega)=[\tilde{\mathcal{K}}(a,1\cdots s;\omega)\,\tilde{\mathcal{K}}^{-1}(a,1;\omega)$$
$$-\mathcal{K}(a,1\cdots s;\omega=\infty)\,\mathcal{K}^{-1}(a,1\cdots s;\omega=\infty)]\tilde{K}(a,1;\omega). \qquad \text{(III-B-36)}$$

The similarity of the above with equations III-B-12 and III-B-17 suggests that the approach used to determine the functional form of $\tilde{V}_c(a,1;\omega)$ from the third equation of the hierarchy will follow that used in Section III-B to find the functional form of $\tilde{M}(\omega)$ from the second equation of the hierarchy.

With the exception of an intermediate step, the algebra involved in converting the third equation of the hierarchy into one for $\tilde{\chi}(a,1,2;\omega)$, defined by equation III-B-35, is similar to that used to convert the second equation of the hierarchy from an equation for $\dot{D}(a,1;t)$ to one for $\tilde{K}(a,1;\omega)$.[32,33] The result of this conversion, determined in Appendix C, is

$$(\omega-L^{(2)})\tilde{\chi}(a,1,2;\omega)+\mathcal{K}(a,1,2;\omega=\infty)\,\mathcal{K}^{-1}(a,1;\omega=\infty)\times$$
$$\times[n\mathrm{Tr}_2\{(L_{ea}(2)+L^{21}_{ee})\tilde{\chi}(a,1,2;\omega)]-n\mathrm{Tr}_3\{(L_{ea}(3)+L^{32}_{ee}+$$
$$+L^{31}_{ee})\tilde{\chi}(a,1,2;\omega)\}=S(a,1,2) \qquad \text{(III-B-37)}$$

where $S(a,1,2)$ is a complicated, frequency independent, source term.

If we further define an operator, $\tilde{W}(a,1,2;\omega)$, as follows,

$$\tilde{W}(a,1,2;\omega)\tilde{\chi}(a,1,2;\omega)=\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\times$$
$$\times n\mathrm{Tr}_2\{(L_{ea}(2)+L_{ee}^{21})\tilde{\chi}(a,1,2;\omega)\}-n\mathrm{Tr}_3\{(L_{ea}(3)+L_{ee}^{31}+$$
$$+L_{ee}^{32})\tilde{\chi}(a,1,2,3;\omega)\ , \qquad \text{(III-B-38)}$$

we can formally solve for $\tilde{\chi}(a,1,2;\omega)$ and $\tilde{V}_c(a,1;\omega)$ in terms of $S(a,1,2)$ and $\tilde{W}(a,1,2;\omega)$:

$$\tilde{\chi}(a,1,2;\omega)=\frac{1}{\omega-L^{(2)}-\tilde{W}(a,1,2;\omega)}S(a,1,2),$$

$$\tilde{V}_c(a,1;\omega)=-in\mathrm{Tr}_2\{(L_{ea}^{(2)}+L_{ee}^{21})\frac{i}{\omega-L^{(2)}-\tilde{W}(a,1,2;\omega)}S(a,1,2)\}, \qquad \text{(III-B-39)}$$

where we recognize that $\tilde{V}_c(a,1;\omega)$ is still formally exact with all the complicated N-body effects hidden in the operator $\tilde{W}(a,1,2;\omega)$.

III-C Short Time Limit

In the next chapter we will consider some possible weak coupling limits to the memory operator, $\tilde{M}(\omega)$. Before we do this, however, it will be useful to consider an alternative approximation method. In equation III-B-10 we rewrote the first equation of the hierarchy in the form:

$$\left(\frac{\partial}{\partial t}+iL_a\right)\vec{D}(a;t)=-iB\vec{D}(a;t)-i\int_0^t dt'M(t'-t)\vec{D}(a;t'), \qquad \text{(III-B-10)}$$

where B represented the singular, time independent part of the collision operator, $\chi(t'-t)$, and $M(t'-t)$ represented its time dependent, nonsingular part. From the Laplace transform of equation III-B-10 we got

$$\tilde{D}(a;\omega)=\frac{i}{\omega-L_a-B-M(\omega)}\rho_a\vec{d}. \qquad \text{(III-B-10)}$$

B was called the short time limit of $\chi(t'-t)$ and $\tilde{M}(\omega)$ vanished in the infinite frequency limit. Hence, the memory operator was divided into a frequency dependent and a frequency independent part. We will see in this section that it is useful to apply the analogous separation to higher order equations in the hierarchy.[35,36]

Equation III-B-11, above, is exact and has the same form as the expressions for $\tilde{M}(\omega)$ and $\tilde{V}_c(a,1;\omega)$ which are also exact:

$$\tilde{M}(\omega)=-inTr_1\{L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega=\infty)-\tilde{V}_c(a,1;\omega)}GL_{ea}(1)\rho^{1}(a)\} \qquad \text{(III-B-28)}$$

$$\tilde{V}_c(a,1;\omega)=-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\frac{i}{\omega-L^{(2)}-\tilde{W}(a,1,2;\omega)}S(a,1,2)\}. \qquad \text{(III-B-39)}$$

Thus, in formally closing the first equation of the hierarchy, we have put all the effects of the N electrons into the atomic operators, B and $\tilde{M}(\omega)$. Similarly, in formally closing the second equation of the hierarchy, we have cast the evaluation of $\tilde{M}(\omega)$ into the form of an effective two body problem (the atom and one electron) where the operators, $V(a,1;\omega=\infty)$ and $\tilde{V}_c(a,1;\omega)$ contain the effects of N-1 electrons. Thus, in both the expression for $\tilde{D}(a;\omega)$ and that for $\tilde{M}(\omega)$ the many body effects have been divided into a short time (infinite frequency) limit and a frequency dependent part that vanishes at t=0 ($\omega=\infty$). The former terms contain mean field effects while the latter contain collisional effects.

Next we consider the physical significance of B and $\tilde{M}(\omega)$ as they appear in the effective atomic resolvent which governs the time development of the operator $\rho_a\vec{d}$, equation III-B-11. If

we were to neglect $\tilde{M}(\omega)$ then all electron-atom effects would be contained in B and the time development of $\rho_a \vec{d}$ would be governed by the mean field electron-atom interactions. The analysis of the separation of $\tilde{V}(a,1;\omega)$ into $V(a,1;\omega=\infty)$ and $\tilde{V}_c(a,1;\omega)$ in equation III-B-28 is very similar. If we were to neglect $\tilde{V}_c(a,1;\omega)$, the time development represented by the resolvent operator, equation III-B-28, would be governed by the exact interaction of the atom with one electron, $L^{(1)}$, plus the mean field effects of the remaining N-1 electrons included in $V(a,1;\omega=\infty)$. Another way of stating this is that the atom is perturbed by a single electron moving in a static background due to the other N-1 electrons.

This discussion suggests a possible systematic approximation method for calculating the line shape function, $I(\omega)$. Keeping only B in the expression for $I(\omega)$ is the crudest approximation and leads only to a slight shift in the location of the line center. Making the approximation at the next level, that is, neglecting only $\tilde{V}_c(a,1;\omega)$ from the denominator of the expression for $\tilde{M}(\omega)$ includes the interaction of the atom with one electron exactly, together with the mean field effects of the other N-1 electrons. It will be observed in the next chapter that most existing theories of electron broadening can be obtained by taking some sort of weak coupling limit of the result of this approximation to $\tilde{M}(\omega)$. It is possible to go further and keep only the short time limit of $\tilde{W}(a,1,2;\omega)$ which appears in the denominator of the expression for $\tilde{V}_c(a,1;\omega)$, but since retaining only $V(a,1;\omega=\infty)$ yields an expression for the memory operator which goes beyond

most existing theories, the nature of $\tilde{V}_c(a,l;\omega)$ will not be emphasized here.

The approximation procedure outlined in this section should be regarded as a possible alternative to the weak coupling limit. It is hoped that this method will serve as a starting point for a fully quantum mechanical unified theory applicable to a high density plasma.

CHAPTER IV
WEAK COUPLING LIMITS

IV-A Introduction

In Section III-C we discussed an exceedingly useful procedure for obtaining approximate line shape functions by taking the short time limits of the different collision operators. In this chapter, however, we will consider a different approximation procedure which, we shall show, parallels more closely the results of existing theories of line broadening. This technique, called the weak coupling limit, involves a perturbation expansion in some sort of coupling parameters; the impact approximation mentioned in Chapter II is related to this technique. In this chapter we identify possible expansion parameters and explore some expansion techniques. We will find that variation in the weak coupling methods lead to different expressions for the memory operator, some of which we will relate to existing theories. One expansion will be developed that leads to an expression for the line shape that contains several of the previously developed theories as approximations, and which can be systematically carried further than any of them.

In Chapter III the results were exact within the limitations of the static ion approximation; neither the classical path nor the no-quenching approximations were made. However, the bulk of the literature concerning line broadening has been within the framework of these approximations, and they will also be assumed

in the remainder of this dissertation. On the other hand it will be shown that several of the important approximations which have been introduced in an ad hoc manner by many authors,[16,17,22,23] the impact approximation, the neglect of electron-electron correlations, and the neglect of electron-atom correlations from the density matrix, will follow from simple expansions of the memory operator in the various coupling parameters.

However, a difficulty that arises in the coupling constant expansion as applied to the line broadening problem in the existence of two intrinsically different types of interactions: the electron-electron interaction and the electron-atom interaction. The electron-electron interaction is treated extensively in the plasma theory literature.[37,38] The electron-atom interaction, however, will contain atomic operators which are unrelated to the fundamental lengths of the usual plasma problem. This suggests that the coupling constant we use for the electron-atom interaction should be independent of the one we use for the electron-electron interaction. In plasma line broadening, the concept of truncating a hierarchy of kinetic equations by expanding simultaneously in two independent parameters was carried out first by Capes and Voslamber.[27] While also using a two parameter expansion, we will employ a different electron-electron coupling parameter and will apply the weak coupling limit in a somewhat different way.

We now discuss possible expansions and expansion parameters further. The most straightforward method is to expand in powers of the coupling constants, λ_{ee} and λ_{ea}, defined by the relations,

$$V_{ae}(j)=\lambda_{ae}V_{ae}(j);\quad L_{ae}(j)=\lambda_{ae}L_{ae}(j); \tag{IV-A-1}$$

$$V_{ee}(j)=\lambda_{ee}V_{ee}(j);\quad L_{ee}(j)=\lambda_{ee}L_{ee}(j). \tag{IV-A-2}$$

This is the approach used by Capes and Voslamber and we will later show that our technique for approximating the kinetic equations gives a result very much like theirs if we go to the same order in the two coupling constants as they did. The expansion in the electron-atom coupling constant is a good one, as seen in Appendix D, and we will use it in this chapter. On the other hand it has been shown in the literature that for large ranges of plasma temperature and density where the electron-electron coupling constant may not be a valid expansion parameter, an expansion in the plasma parameter is the better choice.[37]

The procedure involved in expanding in the coupling constant for an interaction is a simple one which orders contributions to quantities being expanded in powers of that constant. The concept involved in the plasma parameter expansion, however, is slightly more subtle; before the coupling parameter is ever identified, all expressions are first scaled to an appropriate set of units. The natural units with which to scale the plasma problem are

$$\omega_p=(4\pi ne^2/m)^{\frac{1}{2}};\quad L_D=(KT/4\pi ne^2)^{\frac{1}{2}}$$

$$x\to x'=\frac{x}{L_D};\ \omega\to\omega'=\frac{\omega}{\omega_p};\quad v\to v'=\frac{v}{L_D\omega_p}. \tag{IV-A-3}$$

As shown in Appendix D, where the equations involved in the line broadening problem are scaled to these lengths, the appropriate

expansion parameter is the plasma parameter:

$$\Lambda = \frac{1}{4\pi n L_D^3} = \frac{1}{3N} , \qquad \text{(IV-A-4)}$$

where N represents the number of particles in the Debye sphere. It is also observed that if the kinetic equations of line broadening are scaled, the electron-atom coupling parameter becomes

$$\lambda_{ea} = \frac{e^2 a_0}{\omega_p L_D^2 \hbar} . \qquad \text{(IV-A-5)}$$

From Chapter III the line shape due to electron broadening is

$$\tilde{J}(\omega\varepsilon) = \frac{1}{\pi} R_e Tr_a \{\vec{d} \; \frac{i}{\omega - L_a - B - M(\omega)} \rho(a)\vec{d}\} \qquad \text{(IV-A-6)}$$

where the factors, ρ_a, B, and $M(\omega)$, will in general contain terms which include all orders in all of the coupling parameters. Expanding $\rho(a)$, which appears in the numerator to lowest order in λ_{ee} and λ_{ea} is equivalent to replacing it by $e^{-\beta H}/Tr\{e^{-\beta H}\}$, where H_a is the unperturbed atomic Hamiltonian. The resolvent operator $\frac{i}{\omega - L_a - B - \tilde{M}(\omega)}$ is more difficult to approximate, however. A straightforward perturbation expansion which is first order in any of the coupling constants, yields

$$\frac{i}{\omega - L_a - B - \tilde{M}(\omega)} = \frac{i}{\omega - L} \left[1 - i(B + \tilde{M}(\omega))^{(1)} \frac{i}{\omega - L_a}\right] \qquad \text{(IV-A-7)}$$

where $(B + \tilde{M}(\omega))^{(1)}$ represents the lowest order, nonvanishing, term in a perturbation expansion of $B + \tilde{M}(\omega)$. Near the line center, where $\tilde{M}(\omega)$ approaches $M(0)$, the effective atomic resolvent appearing in the line shape function becomes $\frac{i}{\omega - L_a - B - M(0)}$; Since $\frac{i}{\omega - L_a}$

is not necessarily small, an expansion of the form shown in equation IV-A-7 will not be a good one.[39,40] Thus B and $\tilde{M}(\omega)$, which may be viewed as "width and shift" operators for the line shape, should be retained in the denominator; it is then possible to expand B and $\tilde{M}(\omega)$ themselves in the various coupling parameters. In the remainder of this chapter we will discuss the possible methods of expanding them.

From Chapter III we recall that the operators B and $\tilde{M}(\omega)$ are given by

$$B=nTr_1\{L_{ea}(1)\rho(a,1)\rho^{-1}(a) \qquad \text{(III-B-25)}$$

$$\tilde{M}(\omega)=-inTr_1\{L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}\tilde{G}L_{ea}(1)\rho^{-1}(a). \qquad \text{(III-B-28)}$$

The expansion of B in the various coupling parameters is a straightforward problem, but $\tilde{M}(\omega)$, which contains the formally exact operator, $\tilde{V}(a,1;\omega)$, is difficult to deal with. It is the denominator appearing in equation III-B-28 that causes the difficulty. Again, we could expand the resolvent in the manner suggested by equation IV-A-7, but this expansion would also be invalid in the line center. Therefore, we examine the operators in the denominator, $L^{(1)}+\tilde{V}(a,1;\omega)$, in the various weak coupling limits. The results of these approximations to the denominator of the expression for $M(\omega)$ are displayed in Table 1 and are discussed in detail by the remaining sections of this chapter.

TABLE 1. Some Weak Coupling Limits for the Denominator of $\tilde{M}(\omega)$

Some Weak Coupling Limits for the Denominator of $\tilde{M}(\omega)$	RESULT
$\lambda_{ea}=\lambda_{ee}=0$	second order theory no shielding
$\lambda_{ea}=0$; $\Lambda=0$	second order theory "random phase approximation"
$\lambda_{ea}=1$; $\lambda_{ee}=0$	unified theory of VCS
$\lambda_{ea}=1$; $\Lambda=0$ for $\tilde{G}$; $\lambda_{ee}=1$ for denominator of $M(\omega)$	unified theory of Capes and Voslamber
$\lambda_{ea}=1$; $\Lambda=0$	unified theory "random phase approximation"

IV-B Second Order Theories

The simplest class of approximations for G and $\tilde{M}(\omega)$ in equation III-B-28 are those which retain only the lowest order nonvanishing terms in an electron-atom coupling constant expansion. Second order theories are so named because by taking $L^{(1)}+\tilde{V}(a,1;\omega)$ and G to zeroth order in λ_{ea} we restrict the memory operator, $\tilde{M}(\omega)$, to second order in the electron-atom coupling parameter. Even here, however, there is some latitude in approximating the electron-electron interactions; in this section we will consider the cases where $\lambda_{ee}=0$ and $\Lambda=0$.

As the first approximation to both G and $L^{(1)}+\tilde{V}(a,1;\omega)$, we consider $\lambda_{ee}=0$ and $\lambda_{ea}=0$. From equation III-B-8 we have $L^{(1)}=L_a-i\vec{v}_1\cdot\vec{\nabla}_1+L_{ea}(1)$ which to zeroth order in both coupling constants becomes $L^{(1)}-i\vec{v}_1\cdot\vec{\nabla}_1$. The operator, $GL_{ea}(1)\rho^{-1}(a)$, can be simplified if we realize that to lowest order in λ_{ea}, $\rho(a,1)=\rho(a)\rho(1)$ and to lowest order in λ_{ee}, $\rho(1,2)=\rho(1)\rho(2)$. Hence from equation III-B-23

$$GL_{ea}(1)\rho^{-1}(a)=f_0(v_1)\rho(a)L_{ea}(1)\rho^{-1}(a). \qquad \text{(IV-B-1)}$$

Since all contributions to $\tilde{V}(a,1;\omega)$ contain at least one factor of L^{ij}_{ee} or $L^{i}_{ea}(j)$, thus this operator will not contribute in this approximation and $\tilde{M}(\omega)$ becomes:

$$\tilde{M}(\omega)=-in\int d(1)L_{ea}(1)\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1}f_0(v_1)\rho(a)L_{ea}(1)\rho^{-1}(a). \qquad \text{(IV-B-2)}$$

The quantum mechanical analog of this is essentially the expression that was calculated by Smith and Hooper.[18]

Another result is obtained by taking G and $L^{(1)}+\tilde{V}(a,1;\omega)$ to zeroth order in the plasma parameter rather than to zeroth order

in λ_{ee}.[41-43] Again, in this approximation we have $L^{(1)}=L_a-i\vec{v}_1\cdot\vec{\nabla}_1$; but G and $\tilde{V}(a,1;\omega)$ will both be more complicated than they were for the case where $\lambda_{ee}=0$. In equation D-12 of Appendix D the operator $GL_{ea}(1)\rho^{-1}(a)$ is scaled to dimensionless coordinates;

$$G\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p^3L_D^3}[\rho(a)g(a,1)\lambda_{ea}L_{ea}(\vec{r}_1')+\frac{1}{\Lambda}\int d\vec{r}_2'\rho(a)\times$$

$$\times(g(a,1,2)-g(a,1)g(a,1))L_{ea}(\vec{r}_2')]\rho^{-1}(a). \qquad \text{(IV-B-3)}$$

If we now observe that, for $\lambda_{ea}=0$, $g(a,1\cdots s)=g(1\cdots s)$ and if we recall that $H(\vec{r}_1\vec{r}_2)$, defined by $G(\vec{r}_1\vec{r}_2)=1+h(\vec{r}_1\vec{r}_2)$ is the pair distribution function which, when scaled to dimensionless coordinates, is proportional to Λ, then equation D-12 may be written in the form,

$$G\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p^3L_D^3}[\rho(a)\lambda_{ea}L_{ea}(\vec{r}_1')+\int d\vec{r}_2'\rho(a)h(\vec{r}_1'\vec{r}_2')\lambda_{ea}L_{ea}(\vec{r}_2')]\times$$

$$\times\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p^3L_D^3}\rho(a)\lambda_{ea}L_{ea}^s(\vec{r}_1')\rho^{-1}(a)$$

$$L_{ea}^s(\vec{r}_1')=L_{ea}(\vec{r}_1')+\int d\vec{r}_2'h(\vec{r}_1'\vec{r}_2')L_{ea}(\vec{r}_2'). \qquad \text{(IV-B-4)}$$

$L_{ea}^s(\vec{r}_1')$ is an electron-atom interaction which is statically shielded by the electron-electron pair correlation function. In Appendix E it is shown that $K(a,1,2;\omega=\infty|K(a,1;\omega))$ to zeroth order in λ_{ea} is given by

$$K(a,1,2;\omega=\infty|\tilde{K}(a,1;\omega))=f_0(v_1)f_0(v_2)[(1+P_{21})(1+h(12))$$

$$+n\int d(3)f_0(v_2)g(123)P_{31}](1-\hat{C})f_0^{-1}(v_1)\tilde{K}(a,1;\omega).$$

Hence from equation E-16

$$V(a,1;\omega=\infty)=-in\vec{v}_1\cdot\vec{\nabla}_1f_0(v_1)\hat{C}f_0^{-1}(v_1)$$

where

$$\hat{C}=N\int d(2)f_0(v_2)D(12)P_{21};$$

C(12) is the direct correlation function.[45] When this, along with equation IV-B-3, is substituted into the expression for the memory operator we find that

$$\frac{\tilde{M}(\omega)}{\omega_p}=\frac{-i\lambda_{ea}^2}{\Lambda}\int d\vec{r}_1'd\vec{v}_1'L_{ea}(\vec{r}_1')i(\omega'-\frac{L_a}{\omega_p}+i\vec{v}_1'\cdot\vec{\nabla}_1'+in\vec{v}_1'\cdot\vec{\nabla}_1'f_0(v_1')\hat{C}f_0^{-1}(v'))^{-1}\times$$

$$\times\rho(a)f_0(v_1')L_{ea}^s(\vec{v}_1')\rho^{-1}(a). \qquad \text{(IV-B-5)}$$

However, the form of equation IV-B-5 is not simple to evaluate since a modified Vlasov operator,[37] equation E-16, appears in the denominator. We have shown in Appendix F that any expression having the general form of equation IV-B-5 can be cast in the form of a dynamically shielded electron-atom interaction; thus,

$$\frac{\tilde{M}(\omega)}{\omega_p}=\frac{-i\lambda_{ea}}{\Lambda}\int d\vec{v}_1d\vec{v}_1'L_{ea}^D(\vec{r}_1')i(\omega'-\frac{L_a}{\omega_p}+i\vec{v}_1\cdot\vec{\nabla}_1')^{-1}f_0(v_1')\rho(a)\times$$

$$\times L_{ea}(\vec{r}_1')\rho^{-1}(a), \qquad \text{(IV-B-6)}$$

where, in this case, the dynamically shielded interaction is given exactly by equation F-25:

$$L_{ea}^D=\frac{1}{(2\pi)^3}\int d\vec{K}\frac{L_{ea}(\vec{k})}{\varepsilon^{(0)}(\vec{k};\omega-L_a)}e^{-i\vec{k}\cdot\vec{r}}$$

where $(k;\omega-L_a)$ is a frequency dependent dielectric function

$$\varepsilon^{(0)}(\vec{k};\omega-L_a)=[1+\int d\vec{v}_1\frac{i}{\omega-L_a-\vec{v}_1\cdot\vec{k}_1}\vec{v}_1\cdot\vec{k}_1C(k)f_0(v_1)]. \qquad \text{(IV-B-7)}$$

If the static shielding defined by equation IV-B-4 is substituted for the dynamic shielding of equation IV-B-6, we finally arrive

at a second order theory, including electron correlations, similar to that studied by several authors.[19,20,41-43]

IV-C Unified Theories - Expansion in λ_{ee}

Zeroth Order in λ_{ee}

Another useful result is obtained by taking the denominator of the effective two particle resolvent operator in $\tilde{M}(\omega)$ to first order in λ_{ea} and to zeroth order in λ_{ee}. Again, note that it is only the denominator of $\tilde{M}(\omega)$ that we are expanding to first order in λ_{ea} and not the entire function. With this expansion we arrive at an expression for $\tilde{M}(\omega)$ which includes all orders in the interaction of the atom with only one electron. Such an expression for $\tilde{M}(\omega)$ yields a line shape function that is valid in the line wings as well as in the line center; hence, it is called a unified theory. It should be observed that the result obtained in this approximation will entirely neglect electron correlations.

In equation IV-B-1 it was determined that, zeroth order in λ_{ea} and λ_{ee}, G is given by

$$GL_{ea}(1)\rho^{-1}(a)=f_0(v_1)\rho(a)L_{ea}(1)\rho^{-1}(a). \qquad \text{(IV-C-1)}$$

In this approximation the operator $L^{(1)}+\tilde{V}(a,1;\omega)$ is just as simple to evaluate. $L^{(1)}$ is retained in full, while $\tilde{V}(a,1;\omega)=V(a,1;\omega=\infty)+$ $+\tilde{V}_c(a,1;\omega)$, given by equations B-13 and III-B-39, will vanish to zeroth order in λ_{ee} and λ_{ea}. The resulting form for the memory operator is

$$\tilde{M}(\omega)=-in\int d(1)L_{ea}(1)\,\frac{i}{\omega-L_a-L_e(1)-L_{ea}(1)}\,f_0(v_1)\rho(a)L_{ea}(1)\rho^{-1}(a). \qquad \text{(IV-C-2)}$$

The above will be recognized as the same result that was obtained by VCS, whose theory was outlined in Section II-B.[22,23] It will be recalled that their theory used a density expansion of the expression for the memory operator. The advantage of their result was that it included all orders in an expansion of the interaction of the atom with only one electron; while its primary disadvantage was the neglect of the correlation effects of the other N-1 electrons. As mentioned in Section II-B, VCS partially compensate for this neglect by including curoffs in the spatial integrations. In the remainder of this chapter we will show that the mean field effects due to the N-1 additional electrons can be included systematically via an expansion in either λ_{ee} or Λ.

First Order in λ_{ee}

We have just seen the expression that is obtained for the memory operator by taking its denominator to first order in λ_{ea} and zeroth order in λ_{ee}. We next approximate $L^{(1)}+\tilde{V}(a,1;\omega)$ to first order in λ_{ea} or in λ_{ee}.

To first order in λ_{ea}, $L^{(1)}$ is retained in full; but $\tilde{V}(a,1;\omega)$ is complicated and hence must be approximated. The mean field part of this operator, given explictly in Appendix D, equation D-15:

$$V(a,1;\omega=\infty)=n\int d(2)(L_{ea}(2)+L_{ee})\{\rho(a)f_0(v_1)f_0(v_2)[g(a,1,2)(1+P_{21})\times$$

$$+n\int d(3)f_0(v_3)g(a,1,2,3)P_{31}-g(a,1,2)n\int d(2)f_0(v_2)g(a,2)P_{21}]\}\times$$

$$\times\{\rho(a)f_0(v_1)[g(a,1)+n\int d(2)(g(a,1,2)-g(a,1)g(a,2))P_{21}]\}^{-1}$$

$$-n\rho(a)f_0(v_1)g(a,1)\int d(2)L_{ea}(2)P_{21}.$$

We have purposely not written this equation in terms of the dimensionless coordinates related to the plasma parameter because we want to expand it in λ_{ee} not Λ. With the requirement that equation D-15 be taken to first order in either λ_{ea} or λ_{ea}, and since there is an explicit factor of either L_{ee} or L_{ea} appearing under the integral, the remainder of the integrand must be zeroth order in both of the expansion parameters. Under this restriction $g(a,1\cdots s)=1$, and equation D-15 reduces to

$$V(a,1;\omega=\infty)=n\int d(2)L_{ee}^{21}f_0(v_1)P_{21}\equiv V(1) \qquad \text{(IV-C-3)}$$

where $V(1)$ is the usual Vlasov operator and P_{ij} is the permutation operator defined in Appendix B. The collisional term, $\tilde{V}_c(a,1;\omega)$, is given by

$$V_c(a,1;\omega)=-in\int d(2)(L_{ea}(2)+L_{ee}^{21})\frac{i}{\omega-L^{(2)}-\tilde{W}(a,1,2;\omega)}S(a,1,2). \qquad \text{(III-B-39)}$$

It can be shown that $S(a,1,2)$, appearing in the integrand, is first order in either λ_{ea} or λ_{ee}; thus we neglect $\tilde{V}_c(a,1;\omega)$. We now have a result for the denominator of $\tilde{M}(\omega)$ which is exactly the same as that derived by Capes and Vošlamber. If we further take the operator $GL_{ea}(1)\rho^{-1}(a)$ to zeroth order in Λ (not first order in λ_{ee}) the resulting operator is the same as that obtained in Section IV-B:

$$G\frac{L_{ea}(1)}{\omega_p}=\frac{f_0(v_1')}{\omega_p{}^3L_D{}^3}L_{ea}^s(\vec{r}_1')\rho^{-1}(a) \qquad \text{(IV-B-3)}$$

$$L_{ea}^s(\vec{r}_1')=L_{ea}(\vec{r}_1')+\int d\vec{r}_2'\,h(\vec{r}_1'-\vec{r}_2')L_{ea}(\vec{r}_2'). \qquad \text{(IV-B-4)}$$

Substitution of equation IV-C-3, together with equation IV-B-4 into the general expression for the memory operator, equation III-B-28, gives,

$$M(\omega)=-in\int d(1)L_{ea}(1)\frac{i}{\omega-L^{(1)}-V(1)}f_0(v_1)\rho(a)L^s_{ea}\rho^{-1}(a), \qquad \text{(IV-C-4)}$$

which is identical to the result obtained by Capes and Voslamber. If we now apply a technique very similar to the one they used, and which is developed in Appendix F, this equation becomes

$$M(\omega)=-in\int d(1)L^D_{ea}\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L_{ea}(1)}f_0(v_1)\rho(a)L^s_{ea}\rho^{-1}(a) \qquad \text{(IV-C-5)}$$

where the generalized dynamic shielding is given by

$$L^D_{ea}(\vec{r})=\int d\vec{k}d\vec{k}'L_{ea}(-\vec{k})D^{-1}(a,\vec{k},\vec{k}';\omega)e^{-i\vec{k}\cdot\vec{r}}. \qquad \text{(IV-C-6)}$$

It is interesting to note that to lowest order in λ_{ea} the above expression reduces to

$$L^D_{ea}(\vec{r}_1)=\int d\vec{k}'\frac{L_{ea}(-\vec{k})}{\varepsilon(\vec{k};\omega-L_a)}e^{-i\vec{k}\cdot\vec{r}_1}$$

$$\varepsilon(\vec{k};\omega-L_a)=1-\frac{\omega_p^2}{k^2}\int d\vec{v}_1\vec{v}_1\frac{\partial f_0(v_1)}{\partial\vec{v}_1}\frac{i}{\omega-L_a+i\vec{k}\cdot\vec{v}_1}, \qquad \text{(IV-C-6)}$$

where this last quantity has the form of the usual plasma dielectric function, with ω, replaced by $\omega-L_a$.

It should be noted here that the mean field operator appearing in the denominator of equation IV-C-4, and therefore the dynamic shielding of equation IV-C-6, differs slightly from that appearing in the denominator of equation IV-B-5. In that second order theory we took the denominator to zeroth order in the plasma parameter

and derived the generalized Vlasov operator, equation E-16; in this case we have expanded in the electron-electron coupling strength.

IV-D Unified Theory - Random Phase Approximation

In Section IV-A we suggested that for large regions of temperature and density an expansion in the plasma parameter would be preferable to an expansion in the electron-electron coupling strength. We will see in this section that an expansion in this parameter, coupled with an expansion in λ_{ea}, is a distinct improvement over theories presented in previous sections; the result is an all order, or unified, theory in which the effects of electron correlations are systematically accounted for.

Since all operators in this section will be expanded in the plasma parameter we will express them in terms of the dimensionless coordinates x defined in Section IV-A. From Appendix D, equations D-5, D-6, and D-7, we recall that

$$\omega_p \tilde{D}(a;\omega) = i\left(\omega' - \frac{L_a}{\omega_p} - \frac{B}{\omega_p} - \frac{M(\omega)}{\omega_p}\right)^{-1} \rho_a \vec{d},$$

$$\frac{B}{\omega_p} = n\int d(1)\rho(a) f_0(v_1) g(a,1) \frac{L_{ea}(1)}{\omega_p} \rho^{-1}(a),$$

$$\frac{\tilde{M}(\omega')}{\omega_p} = -in\int d(1) \frac{L_{ea}(1)}{\omega_p} \frac{i}{\omega' - \frac{L(1)}{\omega_p} - \frac{\tilde{V}(a,1;\omega)}{\omega_p}} G \frac{L_{ea}(1)}{\omega_p} \rho^{-1}(a).$$

Since the operator B will involve only a static shift, it will not be emphasized in this section; instead we will emphasize a study of $\frac{\tilde{M}(\omega')}{\omega_p}$.

From equation D-12 we can express $G \frac{L_{ea}(1)}{\omega_p} \rho^{-1}(a)$ in

dimensionless units:

$$G\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p{}^3L_D{}^3}\rho(a)\lambda_{ea}g(a,1)L_{ea}(\vec{r}_1')+\frac{1}{\Lambda}\int d\vec{r}_2'\rho(a)g(a,1,2)L_{ea}(\vec{r}_2')$$
$$-g(a,1)\frac{1}{\Lambda}\int d\vec{r}_1'g(a,1)L_{ea}(\vec{r}_1'),$$

where the spatial parts of the reduced distribution functions have not yet been scaled. Since we are requiring that $\frac{GL_{ea}(1)}{\omega_p}\rho^{-1}(a)$ be taken to lowest nonvanishing order in the electron-atom coupling strength, which means that $g(a,1\cdots s)=g(1\cdots s)$, equation D-12 becomes

$$G\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p{}^3L_D{}^3}\rho(a)\lambda_{ea}[L_{ea}(\vec{r}_1')+\frac{1}{\Lambda}\int d\vec{r}_2'g(\vec{r}_1\vec{r}_2)L_{ea}(\vec{r}_2')]\rho^{-1}(a). \qquad \text{(IV-D-1)}$$

It has been shown[44] that reduced distribution functions, when expressed in dimensionless units, may be easily expanded in Λ:

$$g(\vec{r}_1,\vec{r}_2)=1+h(\vec{r}_1,\vec{r}_2)=1+\Lambda h(\vec{r}_1,\vec{r}_2')$$

$$g(\vec{r}_1,\vec{r}_2,\vec{r}_3)=1+h(\vec{r}_1\vec{r}_2)+h(\vec{r}_1\vec{r}_3)+h(\vec{r}_2\vec{r}_3)+h(\vec{r}_1,\vec{r}_2,\vec{r}_3)$$

$$=1+\Lambda h(\vec{r}_1',\vec{r}_2')+\Lambda h(\vec{r}_1'\vec{r}_2')+\Lambda h(\vec{r}_2'\vec{r}_3')+\Lambda^2 h(\vec{r}_1'\vec{r}_2'\vec{r}_3'). \qquad \text{(IV-D-2)}$$

This result may be substituted into equation IV-D-1 with the result

$$G\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\frac{f_0(v_1')}{\omega_p{}^3L_D{}^3}\rho(a)\lambda_{ea}[L_{ea}(\vec{r}_1')+\int d\vec{r}_2'h(r_1'\vec{r}_2')L_{ea}(\vec{r}_2')]\rho^{-1}(a)$$
$$=\frac{f_0(v_1')}{\omega_p{}^3L_D{}^3}\rho_a\lambda_{ea}L^s_{ea}(\vec{r}_1'). \qquad \text{(IV-D-3)}$$

This is the same as the result obtained in Section IV-B.

We must now evaluate $\tilde{V}(a,1;\omega)=V(a,1;\omega=\infty)+\tilde{V}_c(a,1;\omega)$ to first

order in the electron-atom coupling strength and zeroth order in the plasma parameter. It will be convenient to separate this approximation to $\tilde{V}(a,1;\omega)$ into two parts:

$$\tilde{V}(a,1;\omega)=\tilde{V}^{1,0}(a,1;\omega)+\tilde{V}^{0,0}(a,1;\omega). \qquad \text{(IV-D-4)}$$

While $\tilde{V}^{0,0}(a,1;\omega)$ is zeroth order in both λ_{ea} and Λ, $\tilde{V}^{1,0}(a,1;\omega)$ is first order in λ_{ea} and zeroth order in Λ. In Appendix D we have expressed the frequency independent contribution to $\tilde{V}(a,1;)$ in dimensionless units:

$$\frac{V(a,1;\omega=\infty)}{\omega_p}=\int d\vec{r}_2'd\vec{v}_2'\left(\frac{\lambda_{ea}}{\Lambda}L_{ea}(\vec{r}_2')+i\left(\frac{\partial}{\partial\vec{r}_2'}\frac{1}{r_{12}'}\right)\cdot\frac{\partial}{\partial\vec{v}_1'}\right)\{\rho(a)f_0(v_1')f_0(v_2')$$

$$\times[g(a,1,2)(1+P_{21})+\frac{1}{\Lambda}\int d(3')f_0(v_3')(g(a,1,2,3)-g(a,1,2)g(a,3))P_{31})]\}\times$$

$$\times\{\rho(a)f_0(v_1')[g(a,1)+\frac{1}{\Lambda}\int d(2')f_0(v_2')(g(a,1,2)-g(a,1)g(a,2))P_{21}]\}^{-1}$$

$$-\frac{\lambda_{ea}}{\Lambda}g(a,1)\int d\vec{r}_2'd\vec{v}_2'L_{ea}(\vec{r}_2')P_{21}$$

where $L_{ee}^{2'1'}=i\left(\frac{\partial}{\partial\vec{r}_1'}\frac{1}{r_{12}'}\right)\cdot\frac{\partial}{\partial\vec{v}_1'}$. We now identify the terms in the above equation that are zeroth order in both parameters. The terms having integrals containing $L_{ea}(j)$ certainly can't be zeroth order, so we will consider only those terms which do not explicitly contain this factor;

$$V_e^{0,0}(a,1;\omega=\infty)=i\int d\vec{r}_1'd\vec{v}_1'\left(\frac{\partial}{\partial\vec{r}_1'}\frac{1}{r_{12}'}\right)\cdot\frac{\partial}{\partial\vec{v}_1'}\{f_0(v_1')f_0(v_2')$$

$$[g(12)(1+P_{21})+\frac{1}{\Lambda}\int d(3')f_0(v_3')(g(123)-1)P_{31}]\}\{f_0(v_1')$$

$$[1+\frac{1}{\Lambda}\int d(2')f_0(v_2')(g(12)-1)P_{21}]\}^{-1}. \qquad \text{(IV-D-5)}$$

In the last equation we have used the fact that when $\lambda_{ea}\to 0$,

$g(a,1\cdots s)\to g(1\cdots s)$. Equation IV-D-5 will be recognized as the modified Vlasov operator, which in Appendix E, equation E-17, is shown to reduce to

$$V_e^{0,0}(a,1;\omega=\infty)=-in\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)\hat{C}f_0^{-1}(v_1).$$

We must now look at $\tilde{V}_c(a,1;\omega)$, given in dimensionless coordinates by Appendix D (equation D-17),

$$\frac{V_c(a,1;\omega)}{\omega_p}=-i\int d(2')\left(\frac{\lambda_{ea}}{\Lambda}L_{ea}(\vec{r}_2')+i\left(\frac{\partial}{\partial\vec{r}_1'}\frac{1}{r_{12}'}\right)\cdot\frac{\partial}{\partial\vec{v}_1'}\right)\times$$
$$\times i\left(\omega'-\frac{L^{(2)}}{\omega_p}-\frac{\tilde{W}(a,1,2;\omega)}{\omega_p}\right)^{-1}S(a,1,2)$$

in order to determine whether it contributes, to zeroth order in both parameters. The operator, $S(a,1,2)$, given in Appendix C by equation C-11 can be shown to be first order in either λ_{ea} or Λ. Since the free streaming part of the effective resolvent in equation D-17 is zeroth order in both parameters, we see that there will be a contribution to $\tilde{V}_c(a,1;\omega)$ which is first order in λ_{ea} and zeroth order in Λ, but no contribution which is zeroth order in both parameters. Thus we have identified the contribution to $\tilde{V}(a,1;\omega)$ which is zeroth order in both parameters:

$$\tilde{V}^{0,0}(a,1;\omega)=-in\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)Cf_0^{-1}(v_1). \qquad \text{(IV-D-6)}$$

The contributions to $\tilde{V}^{1,0}(a,1;\omega)$ may be determined by examining equations D-16 and D-17 more closely.

The operator $\tilde{V}^{1,0}(a,1;\omega)$ is still very complicated, but there is a class of terms, each having a very simple functional form, that will be seen to have a straightforward physical interpretation. Let us now write out the contributions to $\tilde{V}(a,1;\omega)$

which contain integrals with a factor of $L_{ea}(1)$ in the integrand:

$$\frac{V_a(a,1;\omega=\infty)}{\omega_p} = \int d\vec{r}_1' \cdot d\vec{v}_1' \frac{\lambda_{ea}}{\Lambda} L_{ea}(\vec{r}_1') \{ f_0(v_1') f_0(v_2') [g(12)(1+P_{21})$$

$$+ \frac{1}{\Lambda} \int d(3') f_0(v_3') (g(123)-1) P_{31}] \} \{ f_0(v_1')$$

$$[1 + \int d(2') f_0(r_2') (g(12)-1) P_{21}]^{-1}$$

$$- \frac{\lambda_{ea}}{\Lambda} \int d(2') L_{ea}(r_2') P_{21} \qquad \text{(IV-D-7)}$$

where we have demanded that the above be no more than first order in λ_{ea}. We now substitute equation IV-D-2 into equation IV-D-7 and keep terms no higher than zeroth order in Λ:

$$\frac{V_a(a,1;\omega=\infty)}{\omega_p} = \lambda_{ea} \int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') \{ f_0(v_2') f_0(v_1') [(\frac{1}{\Lambda} + h(\vec{r}_1' \vec{r}_2')) \times$$

$$\times (1+P_{21}) + \int d(3') f_0(v_2') (h(\vec{r}_1' \vec{r}_2') + h(\vec{r}_1' \vec{r}_2') + h(\vec{r}_2' \vec{r}_3') + \Lambda h(\vec{r}_1' \vec{r}_2' \vec{r}_3')$$

$$\times P_{31}] \} (1-\hat{C}) f_0^{-1}(v_1) - \frac{\lambda_{ea}}{\Lambda} \int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') P_{21} \qquad \text{(IV-D-8)}$$

where the results of Appendix E have been utilized. Making use of the symmetry properties of $L_{ea}(j)$, together with the definition of $\hat{C}$, the above equation simplifies:

$$\frac{V_a(a,1;\omega=\infty)}{\omega_p} = \lambda_{ea} \int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') h(\vec{r}_1' \vec{r}_2') f_0(v_2') (1 - f_0(v_1) \hat{C} f_0^{-1}(v_1))$$

$$+ \lambda_{ea} f_0(v_1) \int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') h(\vec{r}_1' \vec{r}_2') (1 - f_0(v_2) \hat{C} f_0^{-1}(v_2) P_{21}$$

$$+ \lambda_{ea} f_0(v_1') \int d\vec{r}_2' d\vec{r}_2' L_{ea}(\vec{r}_2') f_0(v_2') \int d\vec{r}_3' d\vec{v}_3' h(\vec{r}_1' \vec{r}_2' \vec{r}_3') (1 - f_0(v_3) \hat{C} f_0^{-1}(v_3)).$$

(IV-D-9)

From equation IV-D-8 we observe that all but one of the terms contain a permutation operator either explicitly, or implicitly through the operator C. We will separate out these terms and rewrite

equation IV-D-9 in the abbreviated form,

$$\frac{\tilde{V}_a^{1,0}(a,1;\omega=\infty)}{\omega_p} = \lambda_{ea}\int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') h(\vec{r}_1'\vec{r}_2') f_0(v_2') + X(P_{ij}) \qquad \text{(IV-D-10)}$$

where $X(P_{ij})$ represents the contributions that contain P_{ij}. We now combine equation IV-D-10 with the expressions for $\tilde{V}^{0,0}(a,1;\omega)$, $V_e^{1,0}(a,1;\omega=\infty)$, and $\tilde{V}_c^{1,0}(a,1;\omega)$:

$$\frac{\tilde{V}(a,1;\omega)}{\omega_p} \approx -in\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)\hat{C}f_0^{-1}(v_1) + \lambda_{ea}\int d\vec{r}_2' d\vec{v}_2' L_{ea}(\vec{r}_2') h(\vec{r}_1'\vec{r}_2') f_0(v_2') + \tilde{\Delta}(\omega),$$

$$\tilde{\Delta}(\omega) = V_e^{1,0}(a,1;\omega=\infty) + \tilde{V}_c^{1,0}(a,1;\omega) + X(P_{ij}). \qquad \text{(IV-D-11)}$$

In equation IV-D-11 we have explicitly separated out the simple multiplicative frequency independent term, and also the term which is zeroth order in both expansion parameters, from $\frac{\tilde{V}(a,1;\omega)}{\omega_p}$. Hence, $\tilde{\Delta}(\omega)$, which is first order in λ_{ea}, contains integral operators, some of which will be frequency dependent. We now explicitly write out the memory operator, with $\tilde{V}(a,1;\omega)$ given by equation IV-D-11:

$$\frac{\tilde{M}(\omega)}{\omega_p} = -i\frac{\lambda_{ea}^2}{\Lambda}\int d(1')L_{ea}(\vec{r}_1')i\left(\omega' - \frac{L_a}{\omega_p} + i\vec{v}_1'\cdot\vec{\nabla}_1' - \lambda_{ea}L_{ea}^s(\vec{r}_1') + in\vec{v}_1'\cdot\vec{\nabla}_1'\right)^{-1}$$

$$f_0(v_1')\hat{C}f_0^{-1}(v_1') - \tilde{\Delta}(\omega))^{-1}\rho(a)f_0(v_1)L_{ea}^s(\vec{r}_1')\rho^{-1}(a). \qquad \text{(IV-D-12)}$$

where we have recognized that

$$L_{ea}^s(\vec{r}_1') = L_{ea}(\vec{r}_1') + \int d\vec{r}_2' h(\vec{r}_1'\vec{r}_2')L_{ea}(\vec{r}_2'). \qquad \text{(IV-D-13)}$$

This last expression for the memory operator is still not in a particularly convenient form. However, there is a transformation procedure, outlined in Appendix F, that will cast equation IV-E-12 in a form which we can more easily interpret. This technique puts the contributions to the denominator, which are in the form

of integral operators, into a dynamically shielded electron-atom integration. The resulting expression is IV-D-14

$$\frac{M(\omega)}{\omega_p} = -\frac{i\lambda_{ea}^2}{\Lambda}\int d\vec{r}_1' d\vec{v}_1' L_{ea}^D(\vec{r}_1')i(\omega - \frac{L_a}{\omega_p} + i\vec{v}_1'\cdot\vec{\nabla}_1' - \lambda_{ea}L_{ea}^s(\vec{r}_1'))^{-1}$$

$$\rho(a)f_0(v_1')L_{ea}^s(\vec{r}_1')\rho^{-1}(a), \qquad \text{(IV-D-14)}$$

where the dynamically shielded electron-atom interaction is given by equation F-17:

$$L_{ea}^D(\vec{r}) = \int d\vec{k}d\vec{k}' L_{ea}(-\vec{k})D^{-1}(a,\vec{k},\vec{k}';\omega)e^{-i\vec{k}\cdot\vec{r}} .$$

It should be emphasized that no approximation was made in going from equation IV-D-12 to equation IV-D-14. The operator $D^{-1}(a,\vec{k},\vec{k}';\omega)$ includes all of the effects of the operator $\tilde{\Delta}(\omega)$ as well as the effects of the modified Vlasov operator; its functional form may be inferred from equation F-20. Equations IV-E-14 and F-17 give the expression for $\tilde{M}(\omega)$ correct to first order in λ_{ea}. While equation IV-D-14 is exact to that order it is difficult to evaluate in general. However, one simple approximation to $D^{-1}(a,\vec{k},\vec{k}';\omega)$, that keeps only those contributions that are zeroth order in both parameters is particularly useful. Examination of equations F-20 and F-23 indicates that, in this approximation, $D^{-1}(a,\vec{k},\vec{k}';\omega)$ becomes

$$D^{-1}(a,\vec{k},\vec{k}';\omega) = \frac{\delta(\vec{k}'-\vec{k})}{\varepsilon(\vec{k};\omega-L_a)}$$

$$\varepsilon(\vec{k};\omega-L_a) = [1 - \int d\vec{v}_1 \frac{\vec{k}\cdot\vec{v}}{\omega - L_a - \vec{v}_1\cdot\vec{k}} f_0(v_1)C(k)], \qquad \text{(IV-D-15)}$$

which gives for $L^{D}_{ea}(\vec{r}_1)$

$$L^{D}_{ea}(r_1)=\int d\vec{k}e^{-i\vec{k}\cdot\vec{r}_1}\ \frac{L_{ea}(-\vec{k})}{\varepsilon(\vec{k};\omega-L_a)}$$

$\varepsilon(\vec{k};\omega-L_a)$ will be recognized as a generalized dynamic shielding function. It is interesting to further approximate dynamic shielding by static shielding, giving a theory for which all of the interactions are shielded statically. This will be discussed further in the next chapter.

CHAPTER V
DISCUSSION OF RESULTS

V-A Fully Shielded Unified Theory

In Section III-B we developed an expression for the memory operator:

$$M(\omega)=-in\int d(1)L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a). \qquad \text{(III-B-28)}$$

In Section IV-D, $L^{(1)}$ and $\tilde{V}(a,1;\omega)$ were taken to first order in λ_{ea} and all terms in $\tilde{M}(\omega)$ were taken to zeroth order in the plasma parameter:

$$\frac{\tilde{M}(\omega)}{\omega_p}=-i\frac{\lambda_{ea}}{\Lambda}\int d\vec{r}_1 d\vec{v}_1' L_{ea}(\vec{r}_1')i(\omega'-\frac{L_a}{\omega_p}+i\vec{v}_1'\cdot\vec{\nabla}_1'-\lambda_{ea}L^s_{ea}(r_1')$$
$$+in\vec{v}_1'\cdot\vec{\nabla}_1' f_0(v_1')\hat{C}f_0^{-1}(v_1')-\tilde{\Delta}(\omega))^{-1}\rho(a)f_0(v_1')L^s_{ea}(\vec{r}_1')\rho^{-1}(a). \qquad \text{(IV-D-12)}$$

We then proceeded to separate the operators appearing in the denominator into two parts: those containing a factor of the permutation operator, P_{ij}, and those not containing it. The terms containing P_{ij} were combined with the leading $L_{ea}(1)$ to form a dynamically shielded interaction (Appendix F). The remaining terms containing no factor of P_{ij} were left in the denominator to effectively shield the electron-atom interaction appearing there:

$$\frac{M(\omega)}{\omega_p}=\frac{-i\lambda_{ea}^2}{\Lambda}\int d\vec{r}_1' d\vec{v}_1' L^D_{ea}(\vec{r}_1')i(\omega'-\frac{L_a}{\omega_p}+i\vec{v}_1'\cdot\vec{\nabla}_1'-\lambda_{ea}L^s_{ea}(\vec{r}_1'))^{-1}$$
$$\rho(a)f_0(v_1')L^s_{ea}(\vec{r}_1')\rho^{-1}(a). \qquad \text{(IV-D-14)}$$

$$L^D_{ea}(\vec{r}_1)=\int d\vec{k}d\vec{k}' L_{ea}(-\vec{k}')D^{-1}(a,\vec{k},\vec{k}';\omega)e^{-i\vec{k}\cdot\vec{r}_1}$$

where the operator, $D^{-1}(a,\vec{k},\vec{k}';\omega)$, contains all the effects included in $\tilde{\Delta}(\omega)$. In this section we discuss some of the consequences of the functional form of equation IV-D-14.

This result is interesting because it leads to a unified theory in which all of the interactions are shielded. The unified theory of VCS did not explicitly include shielding, while the unified theory of Capes and Voslamber led to an expression for $\tilde{M}(\omega)$ in which only those interactions appearing in the numerator were shielded. The weak coupling limit used to develop equation IV-D-12 is more systematic than that used by either VCS of Capes and Voslamber and leads to the fully shielded result presented here.

As indicated in Section IV-D, a further approximation would be to take the shielding function $D^{-1}(a,\vec{k},\vec{k}';\omega)$ to zeroth order on both Λ and λ_{ea}. This leads to a result similar to that of Capes and Voslamber (Section II-C), except for the static shielding appearing in the denominator. As a further approximation to this last result we replace dynamic shielding by static shielding. This yields an expression for the memory operator in which all of the interactions are statically shielded in the same way:

$$M(\omega)\tilde{=}in\int d(1)L^{s}_{ea}(\vec{r}_1')i(\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L^{s}_{ea}(\vec{r}_1))^{-1}\rho(a)f_0(v_1)L^{s}_{ea}(\vec{r}_1')\rho^{-1}(a),$$

$$L^{s}_{ea}(\vec{r}_1)=L_{ea}(\vec{r}_1)+n\int d(2)f_0(v_2)h(\vec{r}_1\vec{r}_2)L_{ea}(\vec{r}_2), \qquad (IV-A-1)$$

where $h(\vec{r}_1\vec{r}_2)$ is the electron-electron pair correlation function.[44] The fact that all interactions in equation IV-A-1 are the same allows us to integrate by parts, following the procedure of VCS outlined

in Section II-B. Applying this procedure yields

$$\tilde{M}(\omega)=-in(\omega-L_a)\int d\vec{r}_1\, d\vec{v}_1\,[U(t)-1]\,f_0(v_1)(\omega-L_a),$$

$$U(t)=T_{exp}\{-\frac{i}{\hbar}\int_0^t dt' L^s_{ea}(t')\}, \qquad (IV-A-2)$$

where U(t) is the time development operator in the interaction representation and T is the time ordering operator. Equation IV-A-3 closely resembles the expression which VCS evaluated, except that now the electron-atom interaction appearing in the exponential is shielded. VCS evaluated the integral in equation IV-A-2 by neglecting time ordering, assuming that electrons followed straight line trajectories, and cutting off the spatial integrations at the Debye sphere. The numerical results which they obtained using their method have, in general, agreed well with experiment in spite of the ad hoc way in which they accounted for electron correlations. Since an integral over a statically shielded interaction can frequently be approximated with good accuracy, by a bare interaction and some sort of cutoff, we can understand why the procedure employed by VCS was so successful.

V-B Conclusion

In Chapter III we developed a general expression for the line shape function for a dipole radiator immersed in a one component perturbing fluid. The calculation was fully quantum mechanical and it was never necessary for us to specify the nature of either the perturbing fluid or the radiator. A formally exact expression for the line shape was obtained in a form suitable for

approximation. Then in Chapter IV we assumed classical perturbers interacting with the radiator via a Coulomb potential, and we applied the weak coupling limit. It was determined that the weak coupling limit could be applied in a variety of ways and we discovered that we could reproduce several of the existing theories of line broadening, depending on how these limits were used. We also developed a unified theory, which was fully shielded, by expanding $\tilde{M}(\omega)$ to zeroth order in the plasma parameter.

We should emphasize the generality of the method employed here. While we have used some of the ideas of Gross[35] in our development of the short time limit, this work was primarily based on a technique developed by Mazenko[32,33] to study the general problem of time correlation functions. The development of Chapter III was similar to a study of the velocity correlation function made by Mazenko[32] except that we have two different kinds of particles: perturbers and radiators; hence we have two different kinds of interactions. In Chapter IV we restricted our consideration to a plasma for which the classical path approximation was valid, and applied a weak coupling limit based on the nature of these interactions.

We should note, however, that it is , in general, possible to parallel more closely the work of Gross or Mazenko and bypass the weak coupling limit. In Section III-C we discussed the use of short time limits to formally close the BBGKY hierarchy of kinetic equations. Hopefully it will be possible using this approximation procedure, to evaluate a fully quantum mechanical expression for the line shape without applying the weak coupling limit. Such an expression would be necessary to properly treat very dense plasmas, such as laser produced plasmas.[45]

APPENDICES

APPENDIX A
EQUATION FOR $K(a,1;\ )$

In this appendix the second equation of the hierarchy, equation III-A-10, will be put in a form that allows us to formally solve for the operator, $\tilde{K}(a,1;\omega)$, and in turn, to arrive at a formal expression for the memory operator, $\tilde{M}(\omega)$. We have used equation III-B-12, which separates $\vec{D}(a,1;t)$ and $\vec{D}(a,1,2;t)$ into their short time functionals of $\vec{D}(a;t)$ and remainder terms, $\vec{P}(a,1;t)$ and $\vec{P}(a,1,2;t)$, respectively. The result obtained by substituting this separated form into III-A-10 is

$$\left(\frac{\partial}{\partial t}+iL^{(1)}\right)\rho(a,1)\rho^{-1}(a)\vec{D}(a;t)+\left(\frac{\partial}{\partial t}+iL^{(1)}\right)\vec{P}(a,1;t)$$

$$=-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\rho(a,1,2)\rho^{-1}(a)\}\vec{D}(a;t)$$

$$-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{P}(a,1,2;t)\}. \qquad \text{(III-B-22)}$$

We may simplify equation III-B-22 by recalling the first equation of the hierarchy

$$\left(\frac{\partial}{\partial t}+iL_a\right)\vec{D}(a;t)=-inTr_1\{L_{ea}(1)\vec{D}(a,1;t)\}. \qquad \text{(III-A-10)}$$

With the separated expression for $\vec{D}(a,1;t)$ this equation becomes

$$\frac{\partial}{\partial t}\vec{D}(a;t)=-iL_aD(a;t)-inTr_1\{L_{ea}(1)\rho(a;t)\rho^{-1}(a)\}\vec{D}(a;t)$$

$$-inTr_1\{L_{ea}(1)\vec{P}(a;1;t)\} \qquad \text{(A-1)}$$

which, when substituted into equation III-B-22, yields

$$\left(\frac{\partial}{\partial t}+L^{(1)}\right)\vec{P}(a,1;t)+inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{P}(a,1,2;t)\}$$

$$-i\rho(a,1)\rho^{-1}(a)nTr_1\{L_{ea}(1)P(a,1;t)\}=-i\,[L^{(1)}\rho(a,1)$$

$$+nTr_2\{(L_{ea}(2)+L_{ee}^{21})\rho(a,1,2)\}]\rho^{-1}(a)\vec{D}(a;t)$$

$$+i\rho(a,1)\rho^{-1}(a)\,[L_a\rho(a)+nTr_1\{L_{ea}(1)\rho(a,1)\}]\rho^{-1}(a)\vec{D}(a;t). \qquad (A-2)$$

The two terms in brackets on the right hand side of equation A-2 can also be simplified by looking at the first two equations of the equilibrium hierarchy:

$$[L_a\rho(a)+nTr_1\{L_{ea}(1)\rho(a,1)\}]\rho^{-1}(a)\vec{D}(a;t)$$

$$=Tr_{1\cdots N}\{L\rho_{aN}\}\rho^{-1}(a)\vec{D}(a;t) \qquad (A-3)$$

$$[L^{(1)}\rho(a,1)+nTr_2\{(L_{ea}(2)+L_{ee}^{21})\rho(a,1,2)\}]\rho^{-1}(a)\vec{D}(a;t)$$

$$=Tr_{2\cdots N}\{L\rho_{aN}\}\rho^{-1}(a)\vec{D}(a;t). \qquad (A-4)$$

It will be noted that $L\rho_{aN}$ would vanish except for the fact that it operates on a function of atomic coordinates, $\rho^{-1}(a)\vec{D}(a;t)$. The operators, L and ρ_{aN}, will, however, commute; that is, $L\rho_{aN}=\rho_{aN}L$, and we rewrite equations A-3 and A-4,

$$[L_a\rho(a)+nTr_1\{L_{ea}(1)\rho(a,1)\}]\rho^{-1}(a)\vec{D}(a;t)$$

$$=[\rho(a)L_a+nTr_1\{\rho(a,1)L_{ea}(1)\}]\rho^{-1}(a)\vec{D}(a;t) \qquad (A-5)$$

$$[L^{(1)}\rho(a,1)+nTr_2\{(L_{ea}(2)+L_{ee}^{21})\rho(a,1,2)\}]\rho^{-1}(a)\vec{D}(a;t)$$

$$=[\rho(a,1)(L_a+L_{ea}(1))+nTr_2\{\rho(a,1,2)L_{ea}(2)\}]\rho^{-1}(a)\vec{D}(a;t) \qquad (A-6)$$

where we have also made use of the fact that terms with $L_e(j)$ and L_{ee}^{ij}, operating on purely atomic operators, vanish. If equations A-5 and A-6 are substituted into equation A-2 we get

$$(\frac{\partial}{\partial t}+iL^{(1)})\vec{P}(a,1;t)+inTr_2\{(L_{ea}(2)+L_{ee})\vec{P}(a,1,2;t)\}$$

$$-in\rho(a,1)\rho^{-1}(a)Tr_1\{L_{ea}(1)P(a,1;t)\}=-i\rho(a,1)L_{ea}(1)\rho^{-1}(a)\vec{D}(a;t)$$

$$-inTr_2\{\rho(a,1,2)L_{ea}(2)\}\rho^{-1}(a)\vec{D}(a;t)+in\rho(a,1)\rho^{-1}(a)\times$$

$$\times Tr_1\{\rho(a,1)L_{ea}(1)\}\rho^{-1}(a)\vec{D}(a;t). \qquad (A-7)$$

Equation A-7 is useful because with it we have an equation for $\vec{P}(a,1;t)$ and $\vec{P}(a,1,2;t)$ in terms of $\vec{D}(a;t)$. We can define a time independent atomic operator, $GL_{ea}(1)$, given by

$$GL_{ea}(1)\rho^{-1}(a)\vec{D}(a;t)=\rho(a,1)L_{ea}(1)\rho^{-1}(a)D(a;t)+nTr_2\{\rho(a,1,2)L_{ea}(2)$$

$$\times\rho^{-1}(a)\vec{D}(a;t)-n\rho(a,1)\rho^{-1}(a)Tr_1\{\rho(a,1)L_{ea}(1)\}\rho^{-1}(a)D(a;t) \qquad (A-8)$$

with which we can rewrite equation A-7 in a more compact manner;

$$(\frac{\partial}{\partial t}+iL^{(1)})P(a,1;t)+inTr_2\{(L_{ea}(2)+L_{ee}^{21})\vec{P}(a,1,2;t)\}$$

$$-in\rho(a,1)\rho^{-1}(a)Tr_1\{L_{ea}(1)P(a,1;t)\}=-iGL_{ea}(1)\rho^{-1}(a)D(a;t). \qquad (A-9)$$

It is now possible to Laplace transform equation A-9 with the result

$$(\omega-L^{(1)})\tilde{\vec{P}}(a,1;\omega)-nTr_2\{(L_{ea}(2)+L_{ee})\tilde{\vec{P}}(a,1,2;\omega)\}$$

$$+n\rho(a,1)\rho^{-1}(a)Tr_1\{L_{ea}(1)\tilde{\vec{P}}(a,1;\omega)\}=GL_{ea}(1)\rho^{-1}(a)\tilde{\vec{D}}(a;\omega). \qquad (A-10)$$

From equation III-B-16 we recall that $\tilde{\vec{P}}(a,1\cdots s;\omega)=\tilde{K}(a,1\cdots s;\omega)\tilde{\vec{D}}(a;\omega)$ hence we are able to get an equation for $\tilde{K}(a,1;\omega)$;

$$(\omega-L^{(1)})\tilde{K}(a,1;\omega)-inTr_2\{(L_{ea}(2)+L_{ee}^{21})\tilde{K}(a,1,2;\omega)\}$$

$$-n\rho(a,1)\rho^{-1}(a)Tr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\}=GL_{ea}(1)\rho^{-1}(a). \qquad (A-11)$$

Finally in this appendix we will examine the operator $GL_{ea}(1)$, defined by equation A-8, noting that all of the terms on the right hand side of that equation contain a factor of the electron-atom interaction, $L_{ea}(j)$. If we define a permutation operator, P_{ij}, that will change the functional dependence of all operators appearing to its right from functions of particle j coordinates to functions of particle i coordinates, then we can rewrite equation A-8:

$$GL_{ea}\rho^{-1}(a)\vec{D}(a;t)=\rho(a,1)L_{ea}(1)\rho^{-1}(a)\ \vec{D}(a;t)$$

$$+nTr_2\{\rho(a,1,2)P_{21}\}L_{ea}(1)\rho^{-1}(a)\vec{D}(a;t)$$

$$-n\rho(a,1)\rho^{-1}(a)Tr_2\{\rho(a,2)P_{21}\}L_{ea}(1)\rho^{-1}(a)\vec{D}(a;t). \qquad (A-12)$$

Thus we are able to define

$$G=\rho(a,1)+nTr_2\{\rho(a,1,2)P_{21}\}-\rho(a,1)\rho^{-1}(a)nTr_2\{\rho(a,2)P_{21}\}. \qquad (A-13)$$

APPENDIX B
ANALYSIS OF $\tilde{V}(a,1;\omega)$

The purpose of this appendix is to validate equation III-B-26,

$$\tilde{V}(a,1;\omega)\tilde{K}(a,1;\omega)=nTr_2\{L_{ea}(2)+L_{ee})\tilde{K}(a,1,2;\omega)$$
$$-\rho(a,1)\rho^{-1}(a)nTr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)\}, \qquad \text{(III-B-26)}$$

and to study the short time (infinite frequency) limit of $\tilde{V}(a,1;\omega)$. Our first step is to express $\tilde{K}(a,1,2;\omega)$ as some functional of $\tilde{K}(a,1;\omega)$. Following Mazenko[32,33] we will use exactly the same technique for expressing $\tilde{K}(a,1,2;\omega)$ as a functional of $\tilde{K}(a,1;\omega)$ that we used to express $\dot{D}(a,1;t)$ as a functional of $\dot{D}(a;t)$. Equations III-B-5 and III-B-6 suggest that we should attempt to express $\tilde{K}(a,1\cdots s;\omega)$ as a linear map of a function spanning the space of the coordinates of the atom and particle 1 onto the space of the coordinates of the atom and s particles.

First we recall the definition of $\tilde{K}(a,1\cdots s;\omega)$, equation III-B-17,

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{U}(a,1\cdots s;\omega)\tilde{U}^{-1}(a;\omega)-\rho(a,1\cdots s)\rho^{-1}(a). \qquad \text{(III-B-17)}$$

From equations III-B-1 and III-B-3 we have the definitions of $\tilde{U}(a,1\cdots s;\omega)$ and $\tilde{U}(a;\omega)$:

$$\tilde{U}(a,1\cdots s;\omega)=Tr_{s+1\cdots N}\{V^N\frac{i}{\omega-L}\rho_{aN}\}\rho^{-1}(a) \qquad \text{(III-B-1)}$$

$$\tilde{U}(a;\omega)=Tr_{1\cdots N}\{V^N\frac{i}{\omega-L}\rho_{aN}\}\rho^{-1}(a). \qquad \text{(III-B-3)}$$

Making use of the fact that ρ_{aN} and L commute, and substituting equations III-B-1 and III-B-3 into equation III-B-17 we arrive at

$$K(a,1\cdots s;\omega)=Tr_{s+1\cdots N}\{V^N \rho_{aN} \frac{i}{\omega-L}\}\rho^{-1}(a)[Tr_{1\cdots N}\{V^N \frac{i}{\omega-L}\rho_{aN}\}\rho^{-1}(a)]^{-1}-$$

$$-\rho(a,1\cdots s)\rho^{-1}(a). \qquad (B-1)$$

Noting that

$$\tilde{\vec{D}}(a;\omega)= \frac{i}{\omega-L_a-B-\tilde{M}(\omega)}\rho(a)\vec{d} \qquad (III-B-19)$$

$$\tilde{U}(a;\omega)= \frac{i}{\omega-L_a-B-M(\omega)} \qquad (B-2)$$

We can rewrite equation B-1 in a more useful form:

$$K(a,1\cdots s;\omega)=-iTr_{s+1\cdots N}\{\rho_{aN} \frac{i}{\omega-L}\}\rho^{-1}(a)[\omega-L_a-B-\tilde{M}(\omega)]-\rho(a,1\cdots s)\rho^{-1}(a), \qquad (B-3)$$

where B and $M(\omega)$ are given by equations III-B-19 and III-B-28 respectively. We now make use of the identity,

$$\frac{i}{\omega-L} = \frac{i}{\omega-L_a} - \frac{i}{\omega-L} i(L-L_a) \frac{i}{\omega-L_a}, \qquad (B-4)$$

in order to get

$$K(a,1\cdots s;\omega)=-iTr_{s+1\cdots N}\{\rho_{aN}[1- \frac{i}{\omega-L} i \sum_j L_{ea}(j)]\}\frac{i}{\omega-L_a} \times$$

$$\times\rho^{-1}(a)[\omega-L_a-B-M(\omega)]-\rho(a,1\cdots s)\rho^{-1}(a); \qquad (B-5)$$

we have observed that the result of $L_{ea}(j)$ and L_{ee}^{21} operating on purely atomic operators is zero. It would be tempting to cancel $\frac{i}{\omega-L_a}\times(\omega-L_a)$, but we cannot since L_a will not in general commute with $\rho(a)=Tr_{1\cdots N}\{\rho_{aN}\}$. However, from the first equation of the equilibrium hierarchy, equation A-5, we know that

$$\rho^{-1}(a)[L_a+B]=\rho^{-1}(a)[L_a\rho(a)+nTr_1\{L_{ea}(1)\rho(a,1)\}]\rho^{-1}(a)$$

$$=\rho^{-1}(a)[\rho(a)L_a+nTr_1\{\rho(a,1)L_{ea}(1)\}]\rho^{-1}(a)$$

$$=L_a\rho^{-1}(a)+\rho^{-1}(a)nTr_1\{\rho(a,1)L_{ea}(1)\}]\rho^{-1}(a). \qquad (B-6)$$

If this is substituted into equation B-5 we get

$$\tilde{K}(a,1\cdots s;\omega)=-iTr_{s+1\cdots N}\{\rho_{aN}\frac{i}{\omega-L}\Sigma_j L_{ea}(j)\}\rho^{-1}(a)$$

$$+iTr_{s+1\cdots N}\{\rho_{aN}\frac{i}{\omega-L}\}\rho^{-1}(a)[nTr_1\{\rho(a,1)L_{ea}(1)\rho^{-1}(a)+\tilde{M}(\omega)]. \quad (B-7)$$

We now consider equation III-B-28

$$\tilde{M}(\omega)=-inTr_1\{L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a),$$

which we will substitute into equation B-7 and which is consistent with the formal definition of $\tilde{V}(a,1;\omega)$ in equation III-B-26. Now we can extract a factor of $L_{ea}(1)\rho^{-1}(a)$ from all of the terms in equation B-7 by introducing the permutation operator defined in Appendix A. Hence we are able to define the operator, $\tilde{\mathcal{K}}(a,1\cdots s;\omega)$.

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)L_{ea}(1)\rho^{-1}(a)$$

$$\tilde{\mathcal{K}}(a,1\cdots s;\omega)L_{ea}(1)\rho^{-1}(a)=-iTr_{s+1\cdots N}\{\rho_{aN}\frac{i}{\omega-L}\Sigma_j P_{j1}\}L_{ea}(1)\rho^{-1}(a)$$

$$+iTr_{s+1\cdots N}\{\rho_{aN}\frac{i}{\omega-L}\}\rho^{-1}(a)[nTr_2\{\rho(a,1)P_{21}\}L_{ea}(1)\rho^{-1}(a)$$

$$-inTr_2\{L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a)\}. \quad (B-9)$$

We will now assume that $\tilde{\mathcal{K}}(a,1;\omega)$ has an inverse and write

$$\tilde{K}(a,1\cdots s;\omega|\tilde{K}(a,1;\omega))=\tilde{\mathcal{K}}(a,1\cdots s;\omega)\tilde{\mathcal{K}}^{-1}(a,1;\omega)\tilde{K}(a,1;\omega) \quad (B-10)$$

which, when substituted into equation III-B-26, yields

$$\tilde{V}(a,1;\omega)\tilde{K}(a,1;\omega)=nTr_2\{(L_{ea}(2)+L_{ee})\tilde{\mathcal{K}}(a,1;\omega)\tilde{\mathcal{K}}^{-1}(a,1;\omega)\}\tilde{K}(a,1;\omega)$$

$$-\rho(a,1)\rho^{-1}(a)nTr_2\{L_{ea}(2)P_{21}\}\tilde{K}(a,1;\omega)$$

$$\tilde{V}(a,1;\omega)=nTr_2\{(L_{ea}(2)+L_{ee})\tilde{\mathcal{K}}(a,1,2;\omega)\tilde{\mathcal{K}}^{-1}(a,1;\omega)\}$$

$$-\rho(a,1)\rho^{-1}(a)n\mathrm{Tr}_2\{L_{ea}(2)P_{21}\}. \tag{B-11}$$

Thus, we have justified equation III-B-26 and in doing so we have derived an exact formal expression for $\tilde{V}(a,1;\omega)$.

We will now separate $\tilde{V}(a,1;\omega)$ into a frequency dependent and independent part:

$$\tilde{V}(a,1;\omega)=V(a,1;\omega=\infty)+\tilde{V}_c(a,1;\omega); \tag{B-12}$$

$$V(a,1;\omega=\infty)=n\mathrm{Tr}_2\{(L_{ea}(2)+L_{ee}^{21})\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\}$$
$$-\rho(a,1)\rho^{-1}(a)n\mathrm{Tr}_2\{L_{ea}(2)P_{21}\}, \tag{B-13}$$

$$\tilde{V}_c(a,1;\omega)=n\mathrm{Tr}_2\{(L_{ea}(2)+L_{ee}^{21})\tilde{\mathcal{K}}(a,1,2;\omega)\tilde{\mathcal{K}}^{-1}(a,1;\omega)$$
$$-\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\}. \tag{B-14}$$

It is possible to further analyze the expression for $V(a,1;\omega=\infty)$ by realizing that $\lim_{\omega\to\infty}\frac{i}{\omega-L}=\frac{i}{\omega}$. Neglecting terms that are higher than first order in $\frac{i}{\omega}$ from equation B-9 allows us to write

$$\mathcal{K}(a,1\cdots s;\omega=\infty)L_{ea}(1)\rho^{-1}(a)=\frac{1}{\omega}[\mathrm{Tr}_{s+1\cdots N}\{\rho_{aN}\sum_j P_{j1}\}$$
$$-n\rho(a,1\cdots s)\rho^{-1}(a)\mathrm{Tr}_2\{\rho(a,2)P_{21}\}]L_{ea}(1)\rho^{-1}(a). \tag{B-15}$$

When this is substituted into equation B-10 we get

$$\mathcal{K}(a,1\cdots s;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\tilde{K}(a,1;\omega)=[\mathrm{Tr}_{s+1\cdots N}\{\rho_{aN}\sum_j P_{j1}\}$$
$$-n\rho(a,1\cdots s)\rho^{-1}(a)\mathrm{Tr}_2\{\rho(a,2)P_{21}\}][\mathrm{Tr}_{2\cdots N}\{\rho_{aN}\sum_j P_{j1}\}$$
$$-n\rho(a,1)\rho^{-1}(a)\mathrm{Tr}_2\{\rho(a,2)P_{21}\}]^{-1}\tilde{K}(a,1;\omega), \tag{B-16}$$

where it will be noted that the permutation operator, P_{ij}, operates on everything that appears to its right. Hence, we are able to write $V(a,1;\omega=\infty)$ explicitly in terms of known functions, while

the formally exact collisional term, $\tilde{V}_c(a,l;\omega)$, requires the next equation of the hierarchy.

APPENDIX C
KINETIC EQUATION FOR $\tilde{\chi}(a,1,2;\omega)$

In this appendix we will transform the third equation of the hierarchy,

$$\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\vec{D}(a,1,2;t)=-inTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\vec{D}(a,1,2,3;t), \quad \text{(III-A-10)}$$

into an equation for $\tilde{\chi}(a,1,2;\omega)$ defined by equation III-B-36. As in Appendix B we use equation III-B-12 to get

$$\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\rho(a,1,2)\rho^{-1}(a)\vec{D}(a,t)+\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\vec{P}(a,1,2;t)$$

$$=inTr_3\{(L_{ea}(3)+L_{ee}+L_{ee})[\rho(a,1,2,3)\rho^{-1}(a)\vec{D}(a;t)$$

$$+\vec{P}(a,1,2,3;t)]. \quad \text{(C-1)}$$

From the first equation of the hierarchy one obtains

$$\frac{\partial}{\partial t}\vec{D}(a;t)=-iL_a\vec{D}(a;t)-inTr_1\{L_{ea}(1)\rho(a,1)\}\rho^{-1}(a)\vec{D}(a;t)$$

$$-inTr_1\{L_{ea}(1)\vec{P}(a,1;t)\}, \quad \text{(III-A-10)}$$

which can be substituted into equation C-1 to give

$$\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\vec{P}(a,1,2;t)-inTr_1\{L_{ea}(1)\vec{P}(a,1;t)\}$$

$$+inTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\vec{P}(a,1,2,3;t)=-iL^{(2)}\rho(a,1,2)\rho^{-1}(a)D(a;t)$$

$$+\rho(a,1,2)\rho^{-1}(a)L_a\vec{D}(a;t)+i\rho(a,1,2)\rho^{-1}(a)nTr_1\{L_{ea}(1)\rho(a,1)\}$$

$$\rho^{-1}(a)\vec{D}(a;t)-inTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{31})\rho(a,1,2,3)\}\rho^{-1}(a)\vec{D}(a;t).$$

(C-2)

The Laplace transform of equation C-2 yields

$$(\omega-L^{(2)})\tilde{K}(a,1,2;\omega)+nTr_1\{L_{ea}(1)\tilde{K}(a,1;\omega)$$

$$-nTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\tilde{K}(a,1,2,3;\omega)\}=L^{(2)}\rho(a,1,2)\rho^{-1}(a)$$

$$-\rho(a,1,2)\rho^{-1}(a)L_a+nTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\times$$

$$\times\rho(a,1,2,3)\}\rho^{-1}(a)-\rho(a,1,2)\rho^{-1}(a)nTr_1\{L_{ea}(1)\rho(a,1)\}\rho^{-1}(a), \quad (C-3)$$

where we have explicitly used the fact that $\vec{P}(a,1\cdots s;t=0)=0$ and the relation $\vec{P}(a,1\cdots s;\omega)=\tilde{K}(a,1\cdots s;\omega)\tilde{\vec{D}}(a;\omega)$, equations III-B-13 and III-B-16, respectively. It is now useful to take the inverse Laplace transform of equation C-3,

$$\left(\frac{\partial}{\partial t}+iL^{(2)}\right)K(a,1,2;t)-i\rho(a,1,2)\rho^{-1}(a)nTr_3\{L_{ea}(3)K(a,3;t)\}$$

$$=-inTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})K(a,1,23;t)\}, \quad (C-4)$$

where we have noted that

$$K(a,1,2;t=0)=-\rho(a,1,2)\rho^{-1}(a)iL_a+iL^{(2)}\rho(a,1,2)\rho^{-1}(a)$$

$$+inTr_3\{(L_{ea}(3)+L_{ee}^{31}+L_{ee}^{32})\rho(a,1,23)\}\rho^{-1}(a)$$

$$-i\rho(a,1,2)\rho^{-1}(a)nTr_1\{L_{ea}(1)\rho(a,1)\}\rho^{-1}(a). \quad (C-5)$$

Equation C-4 gives a relation between $K(a,1;t)$, $K(a,1,2;t)$, and $K(a,1,2,3;t)$ which will be closed in a manner analogous to that shown in equation III-B-26. We start by using equation III-B-33

$$K(a,1\cdots s;t|K(a,1;t))=K(a,1\cdots s;t=0|K(a,1;t))+X(a,1\cdots s;t) \quad (C-6)$$

where

$$K(a,1\cdots s;t=0|K(a,1;t))=\mathcal{K}(a,1\cdots s;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega)K(a,1;t) \quad (C-7)$$

Again the correspondence between the $t\to 0$ limit and the $\omega\to\infty$ limit should be noted. Equation C-7 may be substituted into equation C-4 with the result that

$$\begin{aligned}&\left(\frac{\partial}{\partial t}+iL^{(2)}\right)\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)K(a,1;t)\\&+\left(\frac{\partial}{\partial t}+iL^{(2)}\right)X(a,1,2;t)-\rho(a,1,2)\rho^{-1}(a)n\mathrm{Tr}_3\{L_{ea}(3)K(a,3;t)\}\\&=-in\mathrm{Tr}_3\{(L_{ea}(3)+L^{31}_{ee}+L^{32}_{ee})[\mathcal{K}(a,1,2,3;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\times\\&\times K(a,1;t)+X(a,1,2,3;t)].\end{aligned} \quad (C-8)$$

Using the inverse Laplace transform of equation A-11, we now eliminate $\frac{\partial}{\partial t}K(a,1;t)$ from equation C-8:

$$\begin{aligned}&\left(\frac{\partial}{\partial t}+iL^{(2)}\right)X(a,1,2;t)+in\mathrm{Tr}_3\{(L_{ea}(3)+L^{31}_{ee}+L^{32}_{ee})X(a,1,2,3;t)\}\\&-i\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)n\mathrm{Tr}_2\{(L_{ea}(2)+L^{21}_{ee})X(a,1,2;t)\}\\&=-iL^{(2)}\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)K(a,1;t)+i\mathcal{K}(a,1,2;\omega=\infty)\times\\&\times\mathcal{K}^{-1}(a,1;\omega=\infty)L^{(1)}K(a,1;t)+\rho(a,1,2)\rho^{-1}(a)n\mathrm{Tr}_3\{L_{ea}(3)K(a,2;t)\}\\&-\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\rho(a,1)\rho^{-1}(a)n\mathrm{Tr}_3\{L_{ea}(3)K(a,3;t)\}\\&+in\mathrm{Tr}_3\{(L_{ea}(3)+L^{31}_{ee}+L^{32}_{ee})[\mathcal{K}(a,1,2,3;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)K(a,1;t)\}\\&+i\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)n\mathrm{Tr}_2\{(L_{ea}(2)+L^{21}_{ee})\mathcal{K}(a,1,2;\omega=\infty)\\&\mathcal{K}^{-1}(a,1;\omega=\infty)K(a,1;t)\}.\end{aligned} \quad (C-9)$$

Since $\tilde{X}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)\tilde{K}(a,1;\omega)$, the Laplace transform of the above equation is

$$(\omega - L^{(2)})\tilde{\chi}(a,1,2;\omega) + \mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\times$$
$$\times n\mathrm{Tr}_2\{(L_{ea}(2)+L^{21}_{ee})\tilde{\chi}(a,1,2;\omega)\} - n\mathrm{Tr}_3\{(L_{ea}(3)+L^{31}_{ee}+L^{32}_{ee})\times$$
$$\times\tilde{\chi}(a,1,2,3;\omega)\} = S(a,1,2) \qquad \text{(C-10)}$$

where $S(a,1,2)$ is a frequency independent, inhomogeneous source term given by

$$S(a,1,2)\tilde{K}(a,1;\omega) = -\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)[L^{(1)}\tilde{K}(a,1;\omega)$$
$$-\rho(a,1)\rho^{-1}(a)n\mathrm{Tr}_2\{L_{ea}(2)\tilde{K}(a,1;\omega)\} + n\mathrm{Tr}_2\{(L_{ea}(2)+L^{21}_{ee})\times$$
$$\times\mathcal{K}(a,1,2;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\tilde{K}(a,1;\omega)] + L^{(2)}\mathcal{K}(a,1,2;\omega=\infty)\times$$
$$\times\mathcal{K}^{-1}(a,1;\omega=\infty)\tilde{K}(a,1;\omega) - \rho(a,1,2)\rho^{-1}(a)n\mathrm{Tr}_3\{L_{ea}(3)\tilde{K}(a,3;\omega)\}$$
$$+ n\mathrm{Tr}_3\{(L_{ea}(3)+L^{31}_{ee}+L^{32}_{ee})\mathcal{K}(a,1,2,3;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\times$$
$$\times\tilde{K}(a,1;\omega). \qquad \text{(C-11)}$$

This is the result needed in order to solve for $\tilde{V}_c(a,1;\omega)$.

APPENDIX D
DIMENSIONLESS UNITS

In order to understand the justification for a plasma parameter expansion, let us first look at the linearized Vlasov equation for a one-component plasma:

$$\left(\frac{\partial}{\partial t}+\vec{v}_1\cdot\vec{\nabla}_1\right)f^{(1)}(\vec{r}_1,\vec{v}_1;t)=\frac{n}{m}\frac{\partial}{\partial\vec{v}_1}f_0(v_1)\int d(2)\,\frac{\partial\phi_{21}}{\partial\vec{r}_1}f^{(1)}(\vec{r}_2,\vec{v}_2;t), \quad \text{(D-1)}$$

where $\phi_{21}\equiv\frac{e^2}{r_{12}}$ is the interparticle potential. In the literature it has been shown that the natural units should be

$$\omega_p=(4\pi ne^2/m)^{\frac{1}{2}};\quad L_D=(KT/4\pi ne^2)^{\frac{1}{2}};$$

$$\omega\to\omega'=\frac{\omega}{\omega_p};\quad x\to x'=\frac{x}{L_D};\quad v\to v'=\frac{v}{L_D\omega_p}. \quad \text{(D-2)}$$

If equation D-1 is scaled with these dimensionless units the result is

$$\left(\frac{\partial}{\partial t'}+\vec{v}_1'\cdot\vec{\nabla}_1'\right)f^{(1)}(\vec{r}_1,\vec{v}_1;t\,)=\frac{ne^2}{\omega_p^2 m}\frac{\partial}{\partial\vec{v}_1'}\cdot f^{(0)}(v_1')\int d(2')\,\frac{\partial}{\partial\vec{r}_1'}\,\frac{1}{r_{12}'}\times$$

$$\times f^{(1)}(\vec{r}_2'\vec{v}_2';t)=\frac{1}{4\pi}\frac{\partial}{\partial\vec{v}_1'}\cdot f_0(v_1')\int d(2')\,\frac{\partial}{\partial\vec{r}_1'}\frac{1}{r_{12}'}f^{(1)}(\vec{r}_1,\vec{v}_1;t). \quad \text{(D-3)}$$

There are two observations that are worth making about equation D-3. The first of these is the fact that whenever L_{ee}^{21} appears in a kinetic equation which is scaled to the dimensionless units defined by equation D-2, it will usually be accompanied by a factor of $\frac{1}{\omega_p}$. The second observation is that, even though the right hand side of the Vlasov equation, equation D-1, is first order in the electron-electron coupling strength, e^2, the right hand side

of equation D-3, when expressed in dimensionless units, is zeroth order in this parameter. Since this term will not be small for long range forces, this suggests that perhaps e^2 is not the natural expansion parameter. Let us examine the following expression:

$$\frac{1}{\omega_p} L_{ee}^{ij} = i \frac{e^2}{\omega_p m} [\vec{\nabla}_{\vec{r}_1} \cdot \vec{\nabla}_{\vec{v}_1} + \vec{\nabla}_{\vec{r}_2} \cdot \vec{\nabla}_{\vec{v}_2}] \frac{1}{r_{12}} = i \frac{e^2}{m\omega_p^2 L_D^3} [\vec{\nabla}_{\vec{r}_1'} \cdot \vec{\nabla}_{\vec{v}_1'} + \vec{\nabla}_{\vec{r}_2'} \cdot \vec{\nabla}_{\vec{v}_2'}] \frac{1}{r_{12}'}$$

$$= \frac{i}{4\pi n L_D^3} [\vec{\nabla}_{\vec{r}_1'} \cdot \vec{\nabla}_{\vec{v}_1'} + \vec{\nabla}_{\vec{r}_2'} \cdot \vec{\nabla}_{\vec{v}_2'}] \frac{1}{r_{12}} = i\Lambda [\vec{\nabla}_{\vec{r}_1'} \cdot \vec{\nabla}_{\vec{v}_1'} + \vec{\nabla}_{\vec{r}_2'} \cdot \vec{\nabla}_{\vec{v}_2'}] \frac{1}{r_{12}'} \qquad (D-4)$$

where we identify $\Lambda = \frac{1}{4\pi n L_D^3}$ as the plasma parameter. For typical experimental temperatures and densities this parameter is about 0.05; this suggests that it might be a good expansion parameter. It should be noticed that, as in the case of the linearized Vlasov equation, the factor of $\frac{1}{\omega_p} L_{ee}$ will often appear under a three dimensional spatial integral and be multiplied by a factor of the density. In this event, the scaling to dimensionless units produces a term which is zeroth order in the plasma parameter but first or higher order in the electron-electron coupling strength; thus, in general, a systematic expansion in the plasma parameter will include different terms than a systematic expansion in the electron-electron coupling strength. The advantages of a plasma parameter expansion over an expansion in the coupling constant for systems with long range forces are discussed in most texts on plasma physics.[37,38]

It will now be useful to rewrite some of the quantities that appear in the line broadening formalism of Chapter III as functions of the dimensionless variables defined by equation D-2:

$$\tilde{\vec{D}}(a;\omega)=\frac{i}{\omega-L_a-B-M(\omega)}\,\rho_a\vec{d} \tag{III-B-17}$$

$$\omega_p\tilde{\vec{D}}(a;\omega)=\frac{i}{\omega'-\frac{L_a}{\omega_p}-\frac{B}{\omega_p}-\frac{\tilde{M}(\omega)}{\omega_p}}\,\rho(a)\vec{d}. \tag{D-5}$$

Note that both B and $M(\omega)$ appear with a factor of $\frac{1}{\omega_p}$

$$\frac{B}{\omega_p}=n\int d(1)\rho(a,1)\,\frac{L_{ea}(1)}{\omega_p}\,\rho^{-1}(a) \tag{D-6}$$

$$\frac{\tilde{M}(\omega)}{\omega_p}=n\int d(1)\,\frac{L_{ea}(1)}{\omega_p}\,\frac{1}{\omega'-\frac{L(1)}{\omega_p}-\frac{\tilde{V}(a,1;\omega)}{\omega_p}}\,G\,\frac{L_{ea}(1)}{\omega_p}\,\rho^{-1}(a) \tag{D-7}$$

where the trace operation of equations III-B-25 and III-B-26 has been replaced by integrals indicating that the classical path approximation has been made. Again, note that every factor of $L_{ea}(j)$ appears with a factor of $\frac{1}{\omega_p}$ which must be taken into account when this operator is scaled:

$$\frac{L_{ea}(1)}{\omega_p}=\frac{e^2}{\omega_p\hbar}\,\frac{\vec{r}_1}{|\vec{r}_1|^3}\cdot\vec{R}=\frac{e^2}{\omega_p L_D^{\,8}}\,\frac{\vec{R}}{\hbar}\cdot\frac{\vec{r}_1}{|\vec{r}_1|^3}. \tag{D-8}$$

If we take R to be approximately the Bohr radius, a_0, then we can define the electron-atom coupling strength to be

$$\lambda_{ea}=\frac{e^2a_0}{\omega_p L_D^2\hbar} \tag{D-9}$$

which, for typical experimental conditions, is about 0.01; hence, we can expect it to be a good expansion parameter.

It is now useful to examine G which is given classically by

$$G\,\frac{L_{ea}(1)}{\omega_p}\rho^{-1}(a)=\rho(a,1)\,\frac{L_{ea}(1)}{\omega_p}\,\rho^{-1}(a)+n\int d(2)\rho(a,1,2)\,\frac{L_{ea}(2)}{\omega_p}\,\rho^{-1}(a)$$
$$-n\rho(a,1)\rho^{-1}(a)\int d(1)\rho(a,1)\,\frac{L_{ea}(1)}{\omega_p}\,\rho^{-1}(a). \tag{D-10}$$

The simplest way to deal with $\rho(a,1\cdots s)$ is to define[30]

$$\rho(a,1\cdots s)=\rho(a)\rho(1)\cdots\rho(s)g(a,1\cdots s)$$

$$\rho(j)=f_0(v_j)/V \qquad \text{(D-11)}$$

where $f_0(v_j)$ is the Maxwell-Boltzman velocity distribution. We will not scale $g(a,1\cdots s)$ here; but it should be noted that to zeroth order in λ_{ea}, $g(a,1\cdots s)\to g(1\cdots s)$, where $g(1\cdots s)$ is the usual spatial reduced distribution function which may easily be expanded in the plasma parameter, Λ.[44] Since $L_{ea}(j)$ is a function of $\vec{r}_j$ only, equation D-10 becomes

$$G\frac{L_{ea}(\vec{r}_1')}{\omega_p}\rho^{-1}(a)=\frac{f_0(\vec{v}_1')}{\omega_p L_D^3}\rho(a)[g(a,1)\lambda_{ea}L_{ea}(\vec{r}_1')+\frac{\lambda_{ea}}{\Lambda}\int d\vec{r}_1'\times$$

$$\times(g(a,1,2)-g(a,1)g(a,2))L_{ea}(\vec{r}_2')] \qquad \text{(D-12)}$$

and when this is substituted into equation D-7, that equation becomes, in dimensionless coordinates,

$$\frac{M(\omega)}{\omega_p}=-\frac{\lambda_{ea}^2}{\omega_p}\int d\vec{v}_1'd\vec{r}_1'L_{ea}(\vec{r}_1')\frac{i}{\omega'-\frac{L_a}{\omega_p}-\frac{\tilde{V}(a,1;\omega)}{\omega_p}}f_0(v_1')\rho(a)\times$$

$$\times[g(a,1)L_{ea}(\vec{r}_1')+\frac{\lambda_{ea}}{\Lambda}\int d\vec{r}_2'(g(a,1,2)-g(a,1)g(a,2))L_{ea}(\vec{r}_2')]\rho^{-1}(a). \qquad \text{(D-13)}$$

All that remains now is to express $L^{(1)}+\tilde{V}(a,1;\omega)$ in dimensionless coordinates. Using equation III-B-8 we get

$$\frac{L^{(1)}}{\omega_p}=\frac{L_a}{\omega}-\frac{i\vec{v}_1\cdot\vec{\nabla}_1}{\omega_p}+\frac{L_{ea}(1)}{\omega_p}=\frac{L_a}{\omega_p}-i\vec{v}_1'\cdot\vec{\nabla}_1'+\lambda_{ea}L_{ea}(\vec{r}_1'). \qquad \text{(D-14)}$$

The operator $\tilde{V}(a,1;\omega)$ will be treated in two parts: the mean field part, $V(a,1;\omega=\infty)$, and the collisional part, $\tilde{V}_c(a,1;\omega)$. The former was given by equation III-B-30

$$V(a,1;\omega=\infty)=n\int d(2)(L_{ea}(2)+L_{ee}^{21})[\rho(a,1,2)(1+P_{21})$$

$$+n\int d(3)\rho(a,1,2,3)P_{31}-n\rho(a,1,2)\rho^{-1}(a)\int d(2)\rho(a,2)P_{21}]\times$$

$$\times[\rho(a,1)+n\int d(2)\rho(a,1,2)P_{31}-n\rho(a,1)\rho^{-1}(a)\int d(2)\rho(a,2)P_{21}]^{-1}$$

$$-\rho(a,1)\rho^{-1}(a)\int d(1)L_{ea}(1)P_{21}. \qquad (D-15)$$

Using equation D-11, the above may be scaled to give

$$\frac{V(a,1;\omega=\infty)}{\omega_p}=\int d\vec{r}_1'd\vec{v}_1'(\frac{\lambda_{ea}}{\Lambda}L_{ea}(\vec{r}_2')+i(\frac{\partial}{\partial\vec{r}_1'}\frac{1}{r_{12}'})\cdot\frac{\partial}{\partial\vec{v}_1'})\{\rho(a)f_0(v_1')f_0(v_2')\times$$

$$\times[g(a,1,2)(1+P_{21})+\frac{1}{\Lambda}\int d(3')f_0(v_3')(g(a,1,2,3)-g(a,1,2)g(a,3))P_{31}]\}\times$$

$$\times\{\rho(a)f_0(v_1')[g(a,1)+\frac{1}{\Lambda}\int d(2')f_0(v_2')(g(a,1,2)-g(a,1)g(a,2))P_{21}]\}^{-1}$$

$$-\Lambda g(a,1)\int d(1')L_{ea}(\vec{r}_1')P_{21}. \qquad (D-16)$$

$\tilde{V}_c(a,1;\omega)$ defined by equation III-B-39,

$$\tilde{V}_c(a,1;\omega)=-in\int d(2)(L_{ea}(2)+L_{ee})\frac{i}{\omega-L^{(2)}-\tilde{W}(a,1,2;\omega)}S(a,1,2) \qquad (III-B-34)$$

is more difficult to scale. It can be shown that all terms in $S(a,1,2)$, given by equation C-12, contain a factor of L_{ea}, L_{ee}, or $(g(12)-1)$ which does not appear under an integral; thus this term is always first order in either λ_{ea} or Λ. In dimensionless coordinates, equation III-B-39 becomes

$$\frac{\tilde{V}_c(a,1;\omega)}{\omega_p}=-i\int d(2')(\frac{\lambda_{ea}}{\Lambda}L_{ea}(\vec{r}_2')+i(\frac{\partial}{\partial r_1'}\frac{1}{r_{12}'})\cdot\frac{\partial}{\partial\vec{v}_1'})$$

$$i(\omega'-\frac{L^{(2)}}{\omega_p}-\frac{\tilde{W}(a,1,2;\omega)}{\omega_p})^{-1}S(a,1,2);$$

$$\frac{L^{(2)}}{\omega_p}=\frac{L}{\omega_p}-i\vec{v}_1'\cdot\vec{\nabla}_1'-i\vec{v}_2'\cdot\vec{\nabla}_2'+i(\vec{\nabla}_{\vec{r}_1'}\cdot\vec{\nabla}_{\vec{v}_1'}+\vec{\nabla}_{\vec{r}_2'}\cdot\vec{\nabla}_{\vec{v}_2'})+\lambda_{ea}L_{ea}(\vec{r}_1')+\lambda_{ea}L_{ea}(\vec{r}_2')$$

(D-17)

showing that $\tilde{V}_c(a,1;\omega)$ is at least first order in λ_{ea} or Λ. Since no real attempt is made to study $\tilde{V}_c(a,1;\omega)$ in this dissertation, other than to identify its order in an expansion in λ_{ea} and Λ, we will not attempt to evaluate $\tilde{W}(a,1,2;\omega)$. It should be noted, however, that to lowest order on both λ_{ea} and Λ, this operator can be evaluated.

APPENDIX E
DIRECT CORRELATION FUNCTION

In Appendix B we obtained the formal result,

$$\tilde{K}(a,1\cdots s;\omega)=\tilde{\mathcal{K}}(a,1\cdots s;\omega)\mathcal{K}^{-1}(a,1;\ )\tilde{K}(a,1;\omega) \qquad (B\text{-}10)$$

with the short time limit,

$$K(a,1\cdots s;\omega=\infty|\tilde{K}(a,1;\omega))=\mathcal{K}(a,1\cdots s;\omega=\infty)\mathcal{K}^{-1}(a,1;\omega=\infty)\tilde{K}(a,1;\omega).$$

The purpose of this appendix is to examine the operator $\mathcal{K}^{-}(a,1;\omega=\infty)$ which appears in the operator $V(a,1;\omega=\infty)$, in the limit $\lambda_{ea}\to 0$. In this limit, $\mathcal{K}(a,1;\omega=\infty)$, defined in equation B-15, becomes:

$$\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a)=\frac{1}{\omega}[\rho(a)f_0(v_1)L_{ea}(1)\rho^{-1}(a)+n\int d(2)\rho(12)$$

$$L_{ea}(2)\rho^{-1}(a)-nf_0(v_1)\int d(1)\rho(a)f_0(v_1)L_{ea}(1)\rho^{-1}(a)], \qquad (E\text{-}1)$$

where the classical limit has also been taken. By taking advantage of the symmetry of $L_{ea}(1)$ we find,

$$\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a)\simeq\frac{1}{\omega}\rho(a)[f(v_1)L_{ea}(1)$$

$$+n\int d(2)\rho(a)f_0(v_2)h(12)L_{ea}(2)]\rho^{-1}(a), \qquad (E\text{-}2)$$

where we recall from Appendix D that

$$\rho(12)=f_0(v_1)f_0(v_2)(1+h(12)). \qquad (D\text{-}11)$$

Equation E-2 is not yet in a convenient form to determine its inverse. In order to do this we will Fourier transform E-2

$$FT[\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a) = \frac{1}{\omega}\rho(a)[f_0(v_1)(1+n\int dv_2 h(\vec{k})f_0(v_2)L_{ea}(\vec{k}))]\rho^{-1}(a)$$

$$= \frac{1}{\omega}\rho(a)f_0(v_1)[1+P_v nh(\vec{k})]L_{ea}(k)\rho^{-1}(a) \qquad (E-3)$$

where the operator P_v is defined by

$$P_v F(\vec{r},\vec{v}) = \int d\vec{v} f_0(\vec{v})F(\vec{r},\vec{v}). \qquad (E-4)$$

It is now possible to solve E-3 for $L_{ea}(\vec{k})\rho^{-1}(a)$ with the result

$$L_{ea}(\vec{k})\rho^{-1}(a) = \omega[1+P_v nh(\vec{k})]^{-1}\rho^{-1}(a)f_0^{-1}(v_1)FT[\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a)$$

$$= \omega(1-P_v \frac{nh(\vec{k})}{1+nh(\vec{k})}\rho^{-1}(a)f_0^{-1}(v_1)FT[\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a) \qquad (E-5)$$

where we have used the fact that $P_v^2 = P_v$. We now define the direct correlation function[46] given by

$$nC(\vec{k}) \equiv \frac{nh(\vec{k})}{1+nh(\vec{k})} \qquad (E-6)$$

with the inverse Fourier transform

$$nC(12) = \frac{1}{(2\pi)^3}\int d\vec{k} e^{-i\vec{k}\cdot(\vec{r}_2-\vec{r}_1)} \frac{nh(\vec{k})}{1+nh(\vec{k})}. \qquad (E-7)$$

The inverse transform of E-5 can now be taken with the result:

$$L_{ea}(1)\rho^{-1}(a) = \omega(1-nC)\rho^{-1}(a)f_0^{-1}(v_1)\mathcal{K}(a,1;\omega=\infty)L_{ea}(1)\rho^{-1}(a) \qquad (E-8)$$

$$\hat{C}F(1) \equiv n\int d(2)f_0(v_1)C(12)F(2). \qquad (E-9)$$

We are now able to rewrite equation B-10 in the following form,

$$K(a,1\cdots s;\omega=\infty|K(a,1;\omega)) = \mathcal{K}(a,1\cdots s;\omega=\infty)\omega(1-\hat{C})\rho^{-1}(a)f_0(v_1)\tilde{K}(a,1;\omega). \qquad (E-10)$$

To be consistent, $\mathcal{K}(a,1\cdots s;\omega=\infty)$ must be taken to the same order

in the coupling strength as $\mathcal{K}^{-1}(a,1;\omega=\infty)$, hence E-10 becomes

$$K(a,1\cdots s;\omega=\infty|\tilde{K}(a,1;\omega))=f_0(v_1)f_0(v_2)[(1+P_{21})(1+h(12))+n\int d(3)f_0(v_3)$$

$$g(123)P_{31}](1-\hat{C})f_0^{-1}(v_1)K(a,1;\omega). \qquad \text{(E-11)}$$

Now that we have calculated $K(a,1,2;\omega=\infty|\tilde{K}(a,1;\omega))$ to zeroth order in the electron atom coupling strength we can now calculate $V(a,1;\omega=\infty)$ in the same approximation by substituting E-11 into B-16 and considering only the integral over L_{ee}^{21}

$$V(a,1;\omega=\infty)=n\int d(2)L_{ee}^{21}f_0(v_1)f_0(v_2)[(1+P_{21})(1+h(12))+$$

$$+n\int d(3)f_0(v_3)g(123)P_{31}](1-\hat{C})f_0^{-1}(v_1). \qquad \text{(E-12)}$$

The term containing $g(1,2,3)$ may be rewritten

$$n\int d(2)L_{ee}^{21}f_0(v_1)f_0(v_2)n\int d(3)g(123)f_0(v_3)(1-\hat{C})f_0^{-1}(v_3)\tilde{K}(a,3;\omega)$$

$$=n\int d(2)[n\int d(3)L_{ee}^{31}f_0(v_1)f_0(v_3)g(123)]f_0(v_2)(1-\hat{C})f_0^{-1}(v_2)K(a,2;\omega)$$

(E-13)

$g(1,2,3)$ can be eliminated from equation E-13 by using the second equation of the equilibrium hierarchy:

$$-i(\vec{v}_1\cdot\vec{\nabla}_1+\vec{v}_2\cdot\vec{\nabla}_2)f_0(v_1)f_0(v_2)g(12)+L_{ee}^{21}f_0(v_1)f_0(v_2)g(12)$$

$$=-nf_0(v_2)\int d(3)L_{ee}^{31}f_0(v_1)f_0(v_2)g(123).$$

After integrating this equation over v we get

$$-i\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)g(12)+L_{ee}^{21}f_0(v_1)g(12)=-n\int d(3)L_{ee}^{31}f_0(v_1)f_0(v_3)g(123). \qquad \text{(E-14)}$$

This can now be substituted into E-13 to give

$$n\int d(2)L_{ee}f_0(v_1)f_0(v_2)n\int d(3)g(123)f_0(v_3)(1-\hat{C})f_0^{-1}(v_3)\tilde{K}(a,1;\omega)$$

$$=n\int d(2)[-L_{ee}+i\vec{v}_1\cdot\vec{\nabla}_1]f_0(v_1)f_0(v_2)g(12)(1-\hat{C})f_0(v_2)\tilde{K}(a,1;\omega). \qquad \text{(E-15)}$$

Equation E-15 may now be combined with E-12 to yield

$$V(a,1;\omega=\infty)=in\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)\int d(2)f_0(v_2)g(12)(1-\hat{C})f_0^{-1}(v_2)P_{21}. \quad \text{(E-16)}$$

From the definition of $\hat{C}$, this can be shown to be equivalent to

$$V(a,1;\omega=\infty)=in\vec{v}_1\cdot\vec{\nabla}_1 f_0(v_1)\hat{C}f_0^{-1}(v_1). \quad \text{(E-17)}$$

This is the result obtained by Zwanzig[47] and others for the short time kinetic equation correcting the Vlasov equation.

APPENDIX F
DYNAMIC SHIELDING

The general expression for the memory operator in the classical path approximation is given by

$$\tilde{M}(\omega)=-in\int d(1)L_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a). \qquad \text{(III-B-28)}$$

In Chapter IV we observe that many of the existing classical approximations to the line shape can be obtained by applying some weak coupling limit to this equation. Expressions derived there for the denominator of equation III-B-28 have some terms which contain the permutation operator, P_{ij}. A convenient technique for dealing with expressions of this type is to use them to form a generalized dynamically shielded electron-atom interaction. This allows us to rewrite equation III-B-28 in the form:

$$\tilde{M}(\omega)=-in\int d(1)L^{D}_{ea}(1)\frac{i}{\omega-L^{(1)}-\tilde{V}'(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a) \qquad \text{(F-1)}$$

where $\tilde{V}'(a,1;\omega)$ contains all contributions to $\tilde{V}(a,1;\omega)$ which are not in the form of integral operators, and $L^{D}_{ea}(1)$ contains the rest.

From Section III-B we recall that the memory operator can be written, in the classical path approximation, as

$$\tilde{M}(\omega)=n\int d\vec{r}_1 d\vec{v}_1 L_{ea}(\vec{r}_1)\tilde{K}(a,1;\omega)$$

$$\tilde{K}(a,1;\omega)=\frac{1}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-iL_{ea}(1)-\tilde{V}(a,1;\omega)}\tilde{GL}_{ea}(1)\rho(a). \qquad \text{(F-2)}$$

To show that the form for $\tilde{M}(\omega)$ indicated in equation F-1 is possible,

we will now consider the operator $\tilde{V}(a,1;\omega)$. We will define an operator $\mathcal{L}(a,1,2;\omega)$ such that $\tilde{V}(a,1;\omega)$ becomes

$$\tilde{V}(a,1;\omega)\tilde{F}(a,1;\omega)=\tilde{V}'(a,1;\omega)\tilde{F}(a,1;\omega)+\int d(2)\tilde{\mathcal{L}}(a,1,2;\omega)\tilde{F}(a,1;\omega) \qquad (F\text{-}3)$$

where $\tilde{F}(a,1;\omega)$ is an aribtrary function. We will now specify that $\mathcal{L}(a,1,2;\omega)$ be a function of $\vec{r}_1-\vec{r}_2$ and $\vec{v}_1$ only so that we can rewrite equation F-2 in the form

$$\tilde{V}(a,1;\omega)\tilde{F}(a,1;\omega)=\tilde{V}'(a,1;\omega)\tilde{F}(a,1;\omega)+\int d\vec{r}_2\,\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,\vec{v}_1,\omega)$$

$$\int dv_2\tilde{F}(a,\vec{r}_2,\vec{v}_2,\omega). \qquad (F\text{-}4)$$

The motivation for this restriction, which is valid for all of the approximations to $\tilde{V}(a,1;\omega)$ considered in Chapter IV, comes from equation F-1 in which is is $\int dv_1\tilde{K}(a,1;\omega)$ for which we must actually solve. Then we rewrite equation III-B-28

$$(\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L_{ea}(1)-\tilde{V}'(a,1;\omega))\tilde{K}(a,1;\omega)$$

$$-\int d\vec{r}_2\,\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,\vec{v}_1;\omega)\int d\vec{v}_2\tilde{K}(a,r_2,v_2;\omega)$$

$$=GL_{ea}(1)\rho^{-1}(a). \qquad (F\text{-}5)$$

We now define

$$\tilde{K}^0(a,\vec{r}_1,\vec{v}_1;\omega)=\frac{1}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L_{ea}(1)-\tilde{V}'(a,1;\omega)}GL_{ea}(1)\rho^{-1}(a) \qquad (F\text{-}6)$$

which allows us to rewrite equation F-5,

$$\int d\vec{v}_1\tilde{K}(a,\vec{r}_1,\vec{v}_1;\omega)-\int d\vec{v}_1\int d\vec{r}_2\,\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L_{ea}(1)-\tilde{V}'(a,1;\omega)}\times$$

$$\times\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,\vec{v}_1;\omega)\int d\vec{v}_1\tilde{K}(a,\vec{r}_2,\vec{v}_2;\omega)=\int d\vec{v}_1\tilde{K}^0(a,\vec{r}_1,\vec{v}_1;\omega). \qquad (F\text{-}7)$$

For convenience in notation we will define

$$\tilde{R}(a,\vec{r}_1,\vec{v}_1;\omega)=\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1-L_{ea}(1)-\tilde{V}'(a,1;\omega)} \tag{F-8}$$

We now Fourier transform equation F-7

$$\int d\vec{v}_1\tilde{K}(a,\vec{k},\vec{v}_1;\omega)+\frac{i}{(2\pi)^3}\int dv_1\int dk'\tilde{R}(a,\vec{k}'-\vec{k},\vec{v}_1;\omega)\tilde{\mathcal{L}}(a,\vec{k}',\vec{v}';\omega)\times$$
$$\times\int d\vec{v}_2\tilde{K}(a,\vec{k}',\vec{v}_2;\omega)=\int d\vec{v}_1\tilde{K}^0(a,\vec{k},\vec{v}_1;\omega). \tag{F-9}$$

This allows us to define the operator

$$\tilde{D}(a,\vec{k},\vec{k}';\omega)=\delta(\vec{k}-\vec{k}')+\frac{i}{(2\pi)^3}\int d\vec{v}_1\tilde{R}(a,\vec{k}'-\vec{k},\vec{v}_1;\omega)$$
$$\tilde{\mathcal{L}}(a,\vec{k}',\vec{v};\omega) \tag{F-10}$$

so that equation F-9 may be written,

$$\int d\vec{k}'\tilde{D}(a,\vec{k},\vec{k}';\omega)\int d\vec{v}_1\tilde{K}(a,\vec{k}',\vec{v}_1;\omega)=\int d\vec{v}_1\tilde{K}^0(a,\vec{k},\vec{v}_1;\omega). \tag{F-11}$$

Now we define

$$\int d\vec{k}''\tilde{D}^{-1}(a,\vec{k},\vec{k}'';\omega)\tilde{D}(a,\vec{k},\vec{k}';\omega)=\delta(\vec{k}-\vec{k}') \tag{F-12}$$

with the useful result

$$\int d\vec{v}_1\tilde{K}(a,\vec{k},\vec{v}_1;\omega)=\int d\vec{k}'\tilde{D}^{-1}(a,\vec{k},\vec{k}';\omega)\int d\vec{v}_1\tilde{K}^0(a,\vec{k}_1',\vec{v}_1;\omega). \tag{F-13}$$

In order to utilize equation F-13 we note that equation F-1 can be rewritten in the form

$$\tilde{M}(\omega)=-\frac{in}{(2\pi)^3}\int d\vec{k}L_{ea}(-\vec{k})\int d\vec{v}_1\tilde{K}(a,\vec{k},\vec{v}_1;\omega). \tag{F-14}$$

We can now substitute F-13 into F-14 to get

$$\tilde{M}(\omega)=-\frac{in}{(2\pi)^3}\int d\vec{k}'\left[\int d\vec{k}L_{ea}(-\vec{k})\tilde{D}^{-1}(a,\vec{k},\vec{k}';\omega)\right]\int dv_1\tilde{K}^0(a,k',\vec{v}_1';\omega) \tag{F-15}$$

with the inverse Fourier transform

$$\tilde{M}(\omega)=in\int d\vec{r}_1 L^D_{ea}(\vec{r}_1)\int d\vec{v}_1 \tilde{K}^0(a,\vec{r}_1,\vec{v}_1;\omega)$$

$$=-in\int d\vec{r}_1 L^D_{ea}(\vec{r}_1)\frac{i}{\omega-L_a-L_e(1)-L_{ea}(1)-\tilde{V}'(a,1;\omega)} GL_{ea}(1)\rho^{-1}(a): \quad (F-16)$$

$L^D_{ea}(r)$, the generalized dynamically shielded electron atom interaction, is defined by

$$L^D_{ea}(\vec{r}_1)=\frac{1}{(2\pi)^3}\iint d\vec{k}d\vec{k}' e^{-i\vec{k}\cdot\vec{r}} L_{ea}(-\vec{k}')\tilde{D}^{-1}(\vec{k}',\vec{k};\omega). \quad (F-17)$$

The form of equation F-15 is particularly useful because it incorporates all of the effects of the difficult mean field integral operators contained in $\tilde{\ }(a,1,2;\omega)$ into the dynamic shielding operator, $\tilde{D}^{-1}(a,\vec{k},\vec{k}';\omega)$.

The shielding supplied by G, in the case of the electron-atom interaction appearing in the numerator, and by $\tilde{V}'(a,1;\omega)$ in the denominator is easy to calculate in the weak coupling limit, and is discussed in Chapter IV. On the other hand the dynamic shielding of $L^D_{ea}(r)$ is more difficult and requires a more complicated approximation procedure. We start by noting that $S(a,\vec{r}_1,v_1';\omega)$ may be written;

$$\tilde{F}(a,\vec{r}_1,\vec{v}_1;\omega)=\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1}-\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1} i(L_{ea}(1)+\tilde{V}(a,1;\omega))\times$$

$$\times R(a,r_1,v_1;\omega) \quad (F-18)$$

which in turn allows us to rewrite the second term on the left hand side of equation F-5:

$$\int d\vec{v}_1\int d\vec{r}_2\ \tilde{R}(a,\vec{r}_1,\vec{v}_1;\omega)\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,\vec{v}_1;\omega)\int dv_2\tilde{K}(a,\vec{r}_2,\vec{v}_2;\omega)=\int d\vec{v}_1\frac{i}{\omega-L_a+i\vec{v}_1\cdot\vec{\nabla}_1}\times$$

$$\int d\vec{r}_2\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,\vec{v}_1;\omega)\int d\vec{v}_2\tilde{K}(a,\vec{r}_2,\vec{v}_2;\omega)-i\int d\vec{v}_1\int d\vec{r}_1\frac{i}{\omega-L_a+I\vec{v}_1\cdot\vec{\nabla}_1}$$

$$(L_{ea}(r_1)+\tilde{V}'(a,1;\omega))R(a,\vec{r}_1,\vec{v}_1;\omega)\mathcal{L}(a,\vec{r}_2-\vec{r}_1;\omega)\int d\vec{v}_2\tilde{K}(a,r_2v_2;\omega). \quad \text{(F-19)}$$

This can be Fourier transformed with the result

$$FT\int d\vec{v}_1\int d\vec{r}_2\tilde{R}(a,\vec{r}_1,\vec{v}_1;\omega)\tilde{\mathcal{L}}(a,\vec{r}_2-\vec{r}_1,v_1;\omega)\int dv_2\tilde{K}(a,\vec{r}_2,\vec{v}_2;\omega)$$

$$=\int dv\ \frac{i}{\omega-L_a+\vec{v}_1\cdot\vec{k}}\tilde{\mathcal{L}}(a,k,\vec{v}_1;\omega)\int d\vec{v}_2\tilde{K}(a,\vec{k},\vec{v}_2;\omega)-\frac{i}{(2\pi)^6}\int d\vec{v}_1d\vec{k}'d\vec{k}''$$

$$\frac{i}{\omega-L_a+\vec{v}_1\cdot\vec{k}}L_{ea}(\vec{k}-\vec{k}'')\tilde{R}(a,\vec{k}''-\vec{k}',\vec{v}_1;\omega)\tilde{\mathcal{L}}(a,\vec{k}',\vec{v}_1;\omega)\int dv_2\tilde{K}(a,\vec{k}',\vec{v}_2;\omega). \quad \text{(F-20)}$$

Combining this result with equation F-8, F-9, and F-10 suggests that $\tilde{D}(a,k,k';\omega)$ should be divided into two parts: one which is local in k-space and one which is nonlocal,

$$\tilde{D}(a,\vec{k},\vec{k}';\omega)=\tilde{D}^{(0)}(a,\vec{k},\vec{k}';\omega)+D^{(1)}(a,\vec{k},\vec{k}';\omega)$$

$$\tilde{D}^{(0)}(a,\vec{k},\vec{k}';\omega)=\delta(\vec{k}-\vec{k}')\left[1+i\int d\vec{v}_1\frac{i}{\omega-L_a+\vec{V}_1\cdot\vec{k}}\tilde{\mathcal{L}}(a,\vec{k};\omega)\right]=\delta(\vec{k}-\vec{k}')\epsilon(\vec{k};\omega-L_a)$$

$$\tilde{D}^{(1)}(a,\vec{k},\vec{k}';\omega)=\frac{1}{(2\pi)^3}\int d\vec{v}_1d\vec{k}''\frac{i}{\omega-L_a+\vec{v}_1\cdot\vec{k}}L_{ea}(\vec{k}-\vec{k}')\tilde{R}(a,\vec{k}''-\vec{k}',v_1;\omega)$$

$$\times\tilde{\mathcal{L}}(a,\vec{k}',\vec{v}_1;\omega). \quad \text{(F-21)}$$

If we assume that $\epsilon(\vec{k};\omega-L_a)$ the mean field part of $\tilde{V}(a,1;\omega)$ is the Vlasov operator, then $\epsilon(k;\omega-L_a)$ is the usual frequency dependent dielectric constant. We now have:

$$\int d\vec{k}\tilde{D}^{-1}(a,\vec{k},\vec{k}'';\omega)\left[\tilde{D}^{(0)}(a,\vec{k}'',\vec{k}';\omega)+\tilde{D}^{(1)}(a,\vec{k}'',\vec{k}';\omega)\right]=\delta(\vec{k}-\vec{k}') \quad \text{(F-22)}$$

or, using equation F-21

$$\tilde{D}^{-1}(a,\vec{k},\vec{k}';\omega)\epsilon(k;\omega-L_a)+\int d\vec{k}''\tilde{D}^{-1}(a,\vec{k},\vec{k}'';\omega)$$

$$\times D^{(1)}(a,\vec{k}'',\vec{k}';\omega)=\delta(\vec{k}'-\vec{k}) \quad \text{(F-23)}$$

$$\tilde{D}^{-1}(a,\vec{k},\vec{k}';\omega)=\frac{\delta(\vec{k}'-\vec{k})}{\varepsilon(\vec{k};\omega-L_a)}-\frac{1}{\varepsilon(\vec{k};\omega-L_a)}\times$$

$$\times\int d\vec{k}''\tilde{D}^{-1}(a,\vec{k},\vec{k}'';\omega)\tilde{D}^{(1)}(a,\vec{k}'',\vec{k}';\omega). \qquad \text{(F-24)}$$

Thus, using equation F-16, we have a formal expression for the dynamically shielded electron-atom interaction. It should be observed that $D^{(1)}(a,\vec{k}'',\vec{k}';\omega)$ does not contribute to lowest order in the electron-atom coupling strength and equation F-16 becomes

$$L^{D}_{ea}(\vec{r}_1)\approx\frac{1}{(2\pi)^3}\int d\vec{k}e^{-i\vec{k}\cdot\vec{r}}\,\frac{L_{ea}(-k)}{\varepsilon(k;\omega-L_a)}. \qquad \text{(F-25)}$$

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BIOGRAPHICAL SKETCH

Thomas William Hussey was born February 7, 1947, at Marble head, Massachusetts. He attended elementary school in Massachusetts and New Hampshire, and was graduated from Vero Beach High School, at Vero Beach, Florida, in June, 1965. In June, 1969, he received the Bachelor of Science degree with a major in physics from the University of Florida, and in June, 1971, he received the Master of Science degree, also from the University of Florida. Since September, 1969, he has been enrolled in the Graduate School of the University of Florida, and since July, 1971, he has actively pursued the degree of Doctor of Philosophy. Since 1970 he has worked as a graduate teaching assistant and as a graduate research assistant. From September, 1969, through July, 1971, he was enrolled in the ROTC program at the University of Florida and is currently a commissioned Lieutenant in the United States Air Force. He is a member of the American Physical Society and of the American Association of Physics Teachers. Thomas William Hussey is married to Barbara Elaine (Ricker) Hussey and they have one child, Thomas Sherwood Hussey.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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